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THE CONSTITUTION DIAGRAM OF THE
MOLYBDENUM-HAFNIUM BINARY SYSTEM*

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SUMMARY

The molybdenum-hafnium binary system has been determined. The body-centered cubic α -Mo primary solid solution extends to approximately 16.5 at. % Hf at 1000°C and 28 at. % Hf at 2165°C at which temperature it reacts peritectically with liquid to form ϵ -Mo₂Hf, a hexagonal Laves phase of the C36-Cu₂Mg type. A eutectic forms at 1915°C between ϵ -Mo₂Hf and the high-temperature β -Hf body-centered cubic primary solid solution which extends to 58.5 at. % Hf at the eutectic temperature. Between 1910° and 1750° the ϵ -Mo₂Hf structure transforms to the cubic η C15-Cu₂Mg form which reverts back to the original ϵ -Mo₂Hf C36 form below 700°C. β -Hf transforms martensitically to hexagonal close-packed α -Hf at 1950°C, the phase field of the latter being very narrow, ranging from approximately 99.2 to 100 at. % Hf. β -Hf decomposes eutectoidally at 73.5 at. % Hf and 1215°C to form η -Mo₂Hf + α -Hf.

INTRODUCTION

Except for a brief reference to the crystal structure and melting temperature of Mo₂Hf by ELLIOTT¹, no description of the molybdenum-hafnium binary system is given in the literature.

On account of the easily oxidizable nature of the alloying elements and their alloys, coupled with their high melting points and the unusually high temperatures required to produce homogeneity and thermal equilibrium, special atmosphere melting furnaces and vacuum heat treatment furnaces were constructed, the latter being capable of attaining temperatures in the region of 3000°C. In addition, unusual methods of heat treating the powder samples for X-ray diffraction analysis had to be devised along with novel types of etching reagents in order to reveal the microstructures.

EXPERIMENTAL

Materials

The alloying elements were of the highest purity obtainable. The molybdenum was prepared by Mr. R. WIEN of the Westinghouse Research Laboratories' Technology Department by the hydrogen reduction at 1100°C of ammonium molybdate

* Work carried out on Air Force Contract No. AF33(166)-6023, Project No. 7351, on behalf of Nuclear Metals Inc., Concord, Mass.

and subsequently degassed *in vacuo* at 1200°C. An analysis of the reduced powder gave (in p.p.m.): Cr 100, Fe 10, Al 30, Mg 50, Co 30, Mn 50, Si 80, with negligible O₂, C, and N.

The hafnium was supplied by the Atomic Energy Commission in the form of crystal bar prepared by the Van Arkel iodide decomposition method. A typical analysis of the material in p.p.m. was as follows: N 20, C 40, Al 50, Cu 20, Ti 35, W 20, Fe 150, Zr 23,000 (2.3%) Cl 300.

Melting of alloys

Usually alloys were made in the form of 30 g buttons. After carefully weighing the required quantities of powdered molybdenum and fine turnings from the hafnium bar, the mixtures were compressed into small slugs at a pressure of 10 tons/in². These, in the early stages of the work were melted under a vacuum of 10⁻⁵–10⁻⁶ mm Hg by means of a Comenetz-type levitation-melting high frequency induction furnace operating at 400,000 cycles and vacuum cast into a small copper chill mold². It was found, however, that alloys prepared in this manner rarely achieved the requisite degree of homogeneity, and segregated areas and unmelted particles of the original alloying elements were frequently observed in the samples. The method was abandoned and replaced by arc-melting in a Kroll-type furnace using a water-cooled copper hearth, tungsten electrode, and a purified argon atmosphere.

In the arc melting process, care was taken first to evacuate the system to 10⁻⁴ mm Hg using a rotary oil pump. The furnace was then flushed four times with research grade argon, pumping down to 10⁻⁴ mm each time. It was then filled with argon to 1/2 atmosphere pressure and the gas carefully scavenged by melting a 15 g titanium button which was held molten for 3 min. The arc was then played on the sample until the whole mass was completely molten. After allowing to cool, the alloy was turned over and remelted, the operation being repeated at least four times and sometimes as many as six according to the appearance of the button. Not only was this remelting process necessary to obtain complete homogeneity of the finished sample, but it was found that an arc current of more than 350 A was absolutely essential in order to ensure freedom from segregated areas and unmelted particles. Samples prepared in this manner had an excellent, clean, silvery mirror-like appearance, and any alloy showing signs of possible contamination was discarded. To accelerate the homogenizing process, the arc was played on the sample after the final melting operation, and held there for several minutes at a temperature just below the melting point.

Alloy compositions

Originally it was intended to analyse the samples. It was found, however, that the weight losses sustained during the melting process and the subsequent heat treatment procedures were so small, and the X-ray and micrographic results so self-consistent, that little would have been gained by chemical analysis, it being more expedient to remake any alloy of dubious composition or faulty heat treatment.

Some slight losses were sustained, however, when annealing under vacuum for long periods near the solidus temperature, but micrographic examination showed that such losses were invariably confined to a sharply delineated surface layer, the thickness of which was at most only a few thousandths of an inch. This impoverish-

ed layer was always removed prior to the preparation of powder samples for X-ray diffraction analysis, thereby ensuring X-ray results which were truly representative of the nominal weighed-out compositions.

Heat treatment of the samples

On account of the very high temperatures required for homogenizing the samples and obtaining thermal equilibrium for phase boundary determinations, conventional wire-wound ceramic-tube furnaces were completely inadequate. The heat-treating techniques ultimately adopted involved the use of a high frequency furnace operating in a vacuum of 10^{-5} to 10^{-6} mm pressure. Inside the coil was a hollow cylindrical molybdenum susceptor having a wall and base thickness of approximately $3/16$ in., the length of the cylinder being 4 in., and its outside diameter $1\frac{3}{4}$ in. approximately. This was closed at its upper end by a molybdenum disc $3/16$ in. in thickness in whose center was drilled a $1/8$ in. diameter spy-hole for observing the specimens within. These latter were stacked in layers on spacers of thin molybdenum sheet.

Micrographic investigation showed that the brief preliminary heat treatment in the argon arc furnace, though helpful, was in itself insufficient to produce a completely homogeneous microstructure. Exploratory anneals in a conventional wire-wound tube furnace indicated that, with the molybdenum alloys in particular, heat treatments of 3 days duration at 1200°C had, for the most part, very little effect. Only when the homogenizing temperatures were raised to about two-thirds of the absolute melting point did the microstructures reveal any marked progress towards the equilibrium structure. The ultimate indication of homogeneity was afforded by the X-ray powder diagrams having well defined high order reflexions, the latter condition being impossible to obtain if coring is present in the lump sample on account of the variation of lattice parameter with composition.

On the basis of experience, homogenization anneals of 24–50 h at 2000°C approximately were employed for α -Mo alloys, dropping to 1750°C for Hf-rich alloys. The equilibrium condition at lower temperatures was obtained after annealing for 3 days or more at the required temperature, but always after the lump had been initially homogenized at the requisite high temperature.

Melting point and temperature measurement techniques

Melting point determinations were made on fully homogenized alloys by the micrographic examination of incipiently melted specimens. The furnace used for this purpose consisted essentially of a thin walled vertical tungsten tube 9 in. long and 1 in. diameter which could be heated to 3000°C by the passage of several hundred amperes. The heater tube was surrounded concentrically by a tantalum radiation shield and the whole assembly was enclosed in a water-cooled chamber approximately 20 in. high and 12 in. diameter and evacuated to 10^{-5} – 10^{-6} mm Hg.

The specimen itself was suspended on a fine wire attached to the mid-point of a fusible fine wire support and located at the mid-point of the heater tube. The specimen could be observed either from above through the open end of the heater or through a $1/8$ in. diameter spy hole drilled through the center of the tube and the radiation shield, thus simulating almost ideal black body conditions. The water-cooled cover of the furnace was fitted with glass observation ports, the windows of which were

protected from condensing metal vapor by means of magnetically operated shutters. Although tungsten wire would seem the obvious material for suspending the Mo-Hf binary alloys in the melting point furnace, it was found unsuitable on account of its tendency to form a low temperature ternary eutectic with the specimens. Since the lowest melting point in the binary Mo-Hf system occurs at the eutectic containing 57 at. % hafnium, it was found convenient to suspend hypoeutectic alloys on wires of pure molybdenum and to suspend hypereutectic alloys on pure hafnium wire which was specially drawn for this purpose.

The first signs of incipient melting were usually given by a gentle swaying motion of the alloy "pendulum". After maintaining at temperature for 5 min, the horizontal wire support was fused by the passage of a high electric current and the falling specimen quenched in a bath of molten tin located below the tungsten tube.

All temperature measurements were made using the same Leeds and Northrup disappearing filament pyrometer which had been specially calibrated at the National Bureau of Standards at temperatures up to 4000°C. Although the reproducibility was of the order of $\pm 5^\circ\text{C}$, the absolute accuracy of the calibration was $\pm 3^\circ$ at 1063°C falling to $\pm 8^\circ$ at 2800°C. On the high range, the uncertainties rose from $\pm 15^\circ$ at 3200°C to $\pm 20^\circ$ at 4000°C.

The apparent emissivity of the 1/8 in. diameter spy-hole was estimated to be 0.994 so that any errors resulting from this slight departure from unity could be neglected. A calculation of the temperature difference between the sample and the walls showed it to be of the order of 1–2°C. This also could be neglected, although we should point out that it was more consistent to sight on the wall behind the specimen rather than on the specimen itself. An important correction, however, is the one which takes into account reflections from the surfaces of the sight glasses in the observation ports and absorption within them. For this purpose it was convenient to employ a correction table computed by RICHARDSON³ using Planck's Law.

TABLE I
PYROMETER CORRECTIONS FOR VARIOUS VALUES OF TRANSMITTANCE

$T_{\text{obs}}(^{\circ}\text{C})$	Correction to be added in $^{\circ}\text{C}$ for transmittance t		
	$t = 0.91$	$t = 0.93$	$t = 0.89$
1500	14	10	17
1600	15	12	19
1700	17	13	21
1800	19	14	23
1900	20	16	25
2000	22	17	27
2100	24	19	30
2200	26	20	33
2300	29	22	35
2400	31	24	38
2500	33	25	41
2600	36	27	44
2700	38	29	47
2800	41	31	51
2900	43	33	54
3000	46	36	57

The corrected temperature T_{true} is given by the expression

$$T_{\text{true}} = \frac{C_2}{\lambda \log_e \left\{ 1 + t \left(\frac{C_2}{e^{\lambda T_{\text{obs}}}} - 1 \right) \right\}} \quad (1)$$

where $C_2 = 14384.7$ micro-degrees, $\lambda = 0.6500$ microns and t is the product of transmittance, reflectance and emissivity of the tube. Using clean, unscratched pyrex glass, the value for t is 0.91. Table I reproduces part of the extensive table of corrections computed by RICHARDSON on the basis of eqn. 1. It shows that for $t = 0.91$ the correction rises from 14° at 1500°C to 46° at 3000°C .

Preparation of microspecimens

Preparation of the micrographs was carried out under the supervision of Mr. R. ANDERSON. All specimens were polished on automatic machines, the general procedure being to grind on silicon carbide papers, rough polish on $6\ \mu$ diamond and finish on Linde B ($0.2\ \mu$ sapphire dust). Samples were then etched electrolytically in the following solutions:

- (1) *Mo etch*, good for Mo-Hf alloys up to $\text{Mo}_{45}\text{Hf}_{55}$

H_2O	100
$\text{K}_2\text{Fe}(\text{CN})_6$	5
KOH	2

- (2) *Lactic acid etch No. 1* — for $\text{Mo}_{50}\text{Hf}_{50}$ to $\text{Mo}_5\text{Hf}_{95}$

Lactic acid	40
HNO_3	40
HF	2

- (3) *Modified lactic acid etch No. 2* — good where No. 1 is too vigorous

Lactic acid	100
HF	1 drop

- (4) *Acetic acid etch* — good where pitting is troublesome with the other etching reagents

Acetic acid	75
HNO_3	25
HF	2

X-ray techniques and sample preparation

X-ray diffraction patterns were taken in a Philips 114.6 mm diameter Debye-Scherrer camera using a high intensity rotating anode demountable crystallographic X-ray tube⁴. Filtered Co $K\alpha$ radiation was employed, the lattice parameters being computed in absolute angstrom units using the well known technique of extrapolating the observed lattice parameters against the function $\frac{1}{2}(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)^{5,6}$, the precision obtained being about one part in 30,000.

The primary function of X-ray diffraction analysis is the identification of the phases in their equilibrium state. Unfortunately, on account of the extremely high temperatures required to remove cold work and promote true equilibrium, the conventional procedures of annealing and quenching powder specimens in evacuated sealed-off thin walled silica capsules could not be used. Consequently, two alternative methods were employed to circumvent these difficulties.

The first of these was to heat-treat the lump samples in the induction furnace until thermal equilibrium was attained, and then radiation quench by switching off.

Alternatively, when the tungsten tube furnace was used, the specimens were allowed to fall *in vacuo* into a bath of molten tin. The heat treated lumps were then crushed and sieved through 400 mesh gauze and X-rayed in the cold worked condition. Although the high order reflexions of the primary solid solutions were somewhat broadened on account of residual lattice distortion, the patterns were sufficiently sharp and well resolved in the lower orders to identify the various constituent phase-structures. Using this method of identification, care had to be taken to ensure that all the crushed powder passed through the sieve, otherwise it was found that the more ductile phase was retained by it and the intensities in the diffraction patterns favored the more brittle constituent and gave an erroneous indication of the balance of the phases.

In the alternative approach, which was employed when accurate lattice parameters were required to fix the solid-solubility limits, use was made of small cylindrical containers which were approximately 3/8 in. in diameter, 1/2 in. high, wall thickness approximately 1/16 in., and equipped with a loosely-fitting lid about 1/16 in. in thickness, the container material being pure molybdenum or pure hafnium according to the end of the system being studied. Powder specimens produced by crushing the heat treated ingots were placed in these containers and heated as rapidly as possible in a vacuum of about 10^{-5} mm to a temperature at which recovery from cold work and recrystallization occurred without appreciable diffusion and grain growth taking place, held there for a few minutes and then radiation cooled by pulling the specimens out of the hot zone of the furnace by means of an electromagnetically operated ram enclosed in the vacuum system. The recovery times and temperatures were found by trial and error, and were usually of the order of 5 min and 1200°C respectively, although in some cases higher temperatures were employed. By this means, excellent diffraction patterns could be obtained from which precise lattice parameters could be determined. In the case of Hf-rich alloys, heat treatments of one month's duration were also carried out at 800° and 700°C. These heat treatments were performed in the conventional manner using sealed evacuated silica capsules.

After heat treatment, powder samples were given an acid solution pickle to check on the possibility of surface impoverishment. Invariably the powder diagrams taken before and after acid attack were identical, thus indicating that the heat treated powders were substantially homogeneous throughout.

MOLYBDENUM-HAFNIUM CONSTITUTION DIAGRAM

The final molybdenum-hafnium diagram is shown in Fig. 1 in which the crosses indicate boundaries established on the basis of lattice parameter determinations. Four single phase fields are of interest. There are:

- (1) the wide body-centered cubic α -Mo primary solid-solution;
- (2) the intermediate phase based on the composition Mo_2Hf ;
- (3) the extensive body-centered cubic β -Hf primary solid-solution based on the high temperature modification of hafnium;
- (4) the restricted phase field of the hexagonal close-packed α -Hf primary solid-solution based on the low temperature modification of hafnium.

These phase fields are described below. A summary of the X-ray, micrographic and melting point data is given in Table II.

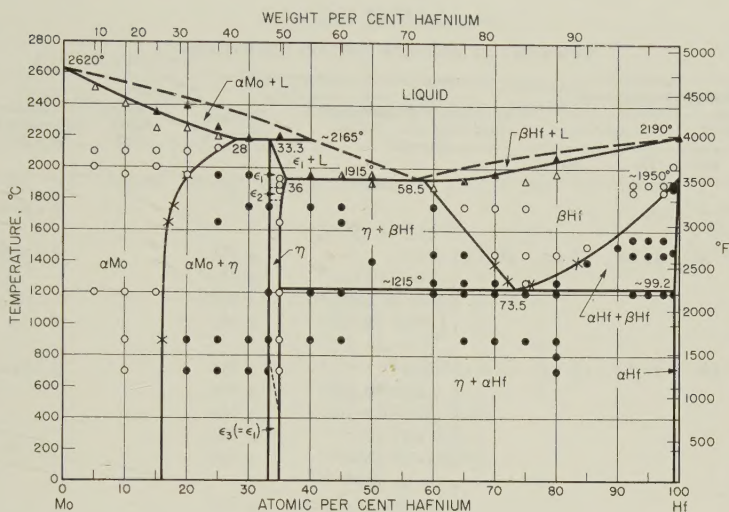


Fig. 1. The molybdenum-hafnium equilibrium diagram.

α -Mo phase field

The α -Mo primary solid-solution extends from pure molybdenum to 28 at.% hafnium at the peritectic temperature of 2165°C. The extent of this phase field decreases rapidly with falling temperature, the solid solubility limit falling to approximately 16.5 at.% hafnium at 900°C. The position of the α -Mo/ $\alpha + \epsilon_1$ boundary at 2100°C was fixed by micrographic examination of quenched alloys, while at lower temperatures it was fixed on the basis of precise lattice parameter determinations supported by micrographic work.

As may be seen from Fig. 2, the lattice parameters of the α -Mo primary solid-solution increase linearly from 3.1470 Å (absolute angstrom units) for pure molybdenum to 3.1992 Å, for an alloy containing 20 at.% hafnium after quenching from 1950°C.

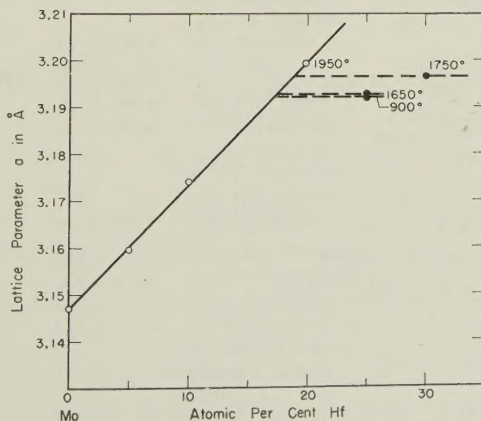
Fig. 2. Lattice parameters of α -Mo Mo-Hf alloys.

TABLE II
SUMMARY OF RESULTS FOR Mo-Hf SYSTEM

Alloy No.	Nominal composition				Heat treatment prior to quench (first temp. gives initial anneal)	Observed structure	Melting point (°C)	Lattice parameters (Å) at 23°C	Vickers hardness No.
	Atomic %		Weight %						
	Mo	Hf	Mo	Hf					
Mo	100	—	100	—				3.1470	
MH19b	95	5	91.08	8.92	48 h at 2000° + 5 min at 2100° + 3 min at 2505° + 1½ h at 1200°	α Mo α Mo α Mo α Mo		3.1596	331
MH10b	90	10	82.87	17.13	24 h at 1950° + 5 min at 2400° + 5 min at 2100° + ½ h at 1200° + 48 h at 900° + 48 h at 900° + 2 weeks slow cool to 700° + 2 weeks at 700°	α Mo α Mo α Mo α Mo α Mo α Mo		3.1740	460
MH20b	84	15	75.28	24.72	48 h at 2000° + 5 min at 2250° + 5 min at 2100° + 1½ h at 1200°	α Mo α Mo α Mo α Mo	2335	3.1905	590
MH11b	80	20	68.25	31.75	24 h at 1950° + 5 min at 2250° + 48 h at 900° + 48 h at 900°, + 2 weeks slow cool to 700°, + 2 weeks at 700°	α Mo α Mo α Mo + η α Mo + ε ₃	2380	3.1992	605
MH21b	75	25	61.72	38.28	48 h at 1650° + 5 min at 2205° + 2 h at 2125° + 5 min at 1950° + 48 h at 900° + 48 h at 900° + 2 weeks slow cool to 700° + 2 weeks at 700°	α Mo + η α Mo α Mo α Mo + ε ₁ α Mo + η α Mo + ε ₃	2235	3.1929 3.1925	731
MH12b	70	30	56.0	44.0	24 h at 1750° + 5 min at 1950° + 48 h at 900° + 48 h 900° + slow cool to 700° in 2 weeks + 2 weeks at 700°	α Mo + η α Mo + ε ₁ α Mo + η α Mo + ε ₃	2165	3.1964	796
MH29b	67	33	52.50	47.50	As-cast 24 h at 1752° + 5 min at 1200° + 48 h at 900° + 48 h at 900°, slow cool in 2 weeks to 700° + 2 weeks at 700°	ε ₁ + α Mo η + α Mo η + α Mo η + α Mo ε ₃ + α Mo.			

TABLE II (continued)

Alloy No.	Nominal composition				Heat treatment prior to quench (first temp. gives initial anneal)	Observed structure	Melting point (°C)	Lattice parameters (Å) at 23°C	Vickers hardness No.
	Atomic %		Weight %						
	Mo	Hf	Mo	Hf					
MH22b(1)	65	35	49.96	50.04	48 h at 1650° + 5 min at 1950°	η ϵ_1	2195	$a = 5.341$ $c = 17.347$ $c/a = 21.624$	858
MH22b(2)	—	—	—	—	17 h at 1910° + 2 $\frac{3}{4}$ h at 1885° + 2 $\frac{1}{2}$ h at 1816° + 5 min at 1200° + 48 h at 900° + 48 h at 900°, slow cool to 700° in 2 weeks + 2 weeks at 700°	ϵ_1 ϵ_1 ϵ_2 η η η		$a = 7.560$	
MH13b	60	40	44.64	55.36	24 h at 1750° + 5 min at 1200° + 48 h at 900°	$\eta + \beta$ Hf $\eta + \alpha$ Hf $\eta + \alpha$ Hf	1935		909
MH23b	55	45	39.65	60.35	48 h at 1650° + 15 min at 1930° + 5 min at 1750° + 5 min at 1200° + 48 h at 900°	$\eta + \beta$ Hf $\epsilon_1 + \beta$ Hf $\eta + \beta$ Hf $\eta + \alpha$ Hf $\eta + \alpha$ Hf			
MH14b	50	50	34.96	65.04	72 h at 1400° + 5 min at 1940°	$\eta + \beta$ Hf $\epsilon_1 + \beta$ Hf			618
MH15b	40	60	26.38	73.62	48 h at 1450° + 5 min at 1875° + 5 min at 1750° + 5 h at 1275° + 5 min at 1200°	$\eta + \beta$ Hf β Hf β Hf + η $\eta + \beta$ Hf $\eta + \alpha$ Hf			637
MH25b	35	65	22.45	77.55	48 h at 1450° + 5 min at 1750° + 5 h at 1275° + 5 min at 1200° + 48 h at 900°	β Hf + η β Hf β Hf + η α Hf + η α Hf + η	1900	3.420	635
MH17b	20	80	11.85	88.15	48 h at 1450° + 5 min at 1960° + 5 h at 1275° + 5 min at 1200° + 48 h at 900° + 48 h at 800° + 48 h slow cool in 2 weeks from 850° + 2 weeks at 700°	β Hf β Hf β Hf + trace α Hf β Hf + α Hf + η α Hf + η α Hf + β Hf + η α Hf + β Hf + η	1945	3.453 3.433 3.368	435
MH27b	15	85	8.66	91.34	72 h at 1400°	α Hf + β Hf		3.648	487
MH32(1)	7.5	92.5	4.18	95.82	48 h at 1550°	α Hf + β Hf			

TABLE II (continued)

Alloy No.	Nominal composition				Heat treatment prior to quench (first temp. gives initial anneal)	Observed structure	Melting point (°C)	Lattice parameters (Å) at 23°C	Vickers hardness No.
	Atomic %		Weight %						
	Mo	Hf	Mo	Hf					
MH ₃₂ (2)					48 h at 1450° + 5 min at 1900° + 5 min at 1850° + 5 min at 1200°	α Hf + β Hf α Hf + β Hf martensitic α Hf + β Hf martensitic α Hf + η			279
MH ₃₀ (1)	5.0	95.0	2.75	97.25	48 h at 1550°	α Hf + β Hf			
MH ₃₀ (2)					48 h at 1450° + 5 min at 1900° + 5 min at 1200°	α Hf + β Hf α Hf + β Hf α Hf + β Hf + η			302
MH ₃₁ (1)	2.5	97.5	1.36	98.64	48 h at 1550°	α Hf + β Hf			361
MH ₃₁ (2)					48 h at 1450° + 5 min at 1900° + 5 min at 1850° + 5 min at 1200°	α Hf + β Hf α Hf + β Hf α Hf + β Hf α Hf + η			
MH ₄₉	1.0	99.0	0.54	99.46	45 h at 2050° + 16 h at 2000° + slow cool to 1900° in 15 min + 30 min 1900° + 3 h at 1880° + 72 h at 1200°	α martensite α martensite trace of primary α + martensite (transformed β) primary α + martensite (transformed β) α Hf + trace η			
Hf 1	—	100	—	100		α Hf β Hf (extrapolated)	2190	a = 3.1969 c = 5.0583 c/a = 1.5822 a = 3.545	

Laves phase-field Mo₂Hf

The Mo₂Hf phase forms at 2154°C *via* a peritectic reaction between the α -Mo primary solid-solution containing 28% hafnium and liquid (of undetermined composition). It is not a true Daltonide, for judging from the slight shifts of the high order reflections in the X-ray powder diagrams, the composition varies somewhat from the stoichiometric ratio 2:1, the total extent not being more than about 1–2 % on either side of the ideal composition.

According to ELLIOTT¹, the melting point of Mo₂Hf is above 2300°C, whereas our own findings place it at 2165°C. The structure of Mo₂Hf between 600 and 2200°C was stated to be isomorphous with the hexagonal C36 type Laves phase MgNi₂, while from 1200 to 1600°C there was evidence of a mixture of the C36-MgNi₂ type with the cubic C15-MgCu₂ modification. The lattice parameters of the C36-MgNi₂

modification were given as $a = 5.341$, $c = 17.347$ Å (from kX), $c/a = 3.248$, while the lattice parameter of the cubic $\text{Cr}_{15}\text{-MgCu}_2$ form was given as $a = 7.577$ Å (from kX).

The present results on the Mo_2Hf phase-field verify the polymorphic nature of the structure, but they differ in detail, partly because of the higher purity of our specimens and partly because the present heat treatments were more conducive to the production of thermal equilibrium.

According to the present investigation, both Mo_2Hf and its neighbor $\text{Mo}_{65}\text{Hf}_{35}$ consist primarily of the hexagonal $\text{C}_{36}\text{-MgNi}_2$ structural type when in the "as-cast" condition. This structure is retained on homogenizing and annealing at 1920 and 1875°C respectively, the phase field occupied by the structure being denoted by ϵ_1 in Fig. 1. On further annealing at 1816°C, the structure of $\text{Mo}_{65}\text{Hf}_{35}$ transforms to a closely related structure which is intermediate between the $\text{C}_{36}\text{-MgNi}_2$ and $\text{Cr}_{14}\text{-MgZn}_2$ types (ϵ_2). This, in turn, transforms to the cubic $\text{Cr}_{15}\text{-MgCu}_2$ modification (η -phase field) on annealing for 24 h at 1752° (*cf.* Table III).

TABLE III
X-RAY DATA ON Mo_2Hf (η -PHASE)

Cubic — $\text{Cu}_2\text{Mg-Cr}_{15}$ — type structure; $a = 7.560$ Å; X-ray density = 11.39 g/cm³; measured density = 11.4 g/cm³; 8 mols/unit cell.

Indices (<i>h, k, l</i>)	<i>Sin</i> ² θ <i>obs.</i>	<i>Sin</i> ² θ <i>calc.</i>	<i>Int.</i> <i>obs.</i>	<i>Int.</i> <i>calc.</i>	<i>d</i>
111			unobs.	1	4.37
200			unobs.	0	
220	0.11212	0.11215	18	18	2.67
311	0.15415	0.15420	45	45	2.28
222	0.16810	0.16823	12	11	2.18
400			unobs.	1	1.82
331			unobs.	1	1.74
420			unobs.	0	
422	0.33626	0.33646	16	16	1.54
511	0.37827	0.37851	30	30	1.46
333					
440	0.44827	0.44860	27	29	1.34
531			unobs.	1	1.28
600			unobs.	0	
442					
620	0.56061	0.56076	12	13	1.196
533	0.60250	0.60282	21	20	1.154
622	0.61678	0.61683	19	15	1.141
444			unobs.	1	1.092
711			unobs.	1	1.059
551					
640			unobs.	0	
642	0.78511	0.78506	36	37	1.011
731	0.82711	0.82712	100	100	0.985
553					
800	0.89720	0.89722	33	33	0.946

Both Mo_2Hf and $\text{Mo}_{65}\text{Hf}_{35}$ remain cubic down to 900°C, but below this temperature the slight compositional difference reveals itself by a difference in behavior. On annealing for 2 weeks at 700°C, $\text{Mo}_{65}\text{Hf}_{35}$ remains cubic, but surprisingly enough

Mo_2Hf transforms to ϵ_3 which possesses the original hexagonal $\text{C}_{36}\text{-MgNi}_2$ structure of the ϵ_1 high temperature phase. However, relief from lattice strain and grain growth must proceed extremely slowly at 700°C , for the high order reflections in the diffraction pattern of the low temperature hexagonal modification of Mo_2Hf are extremely diffuse. Further work on these transformations is proceeding and will be published in due course.

α - and β -Hf phase fields

Hafnium exists in two polymorphic forms. According to ZWIKKER⁷ the low temperature hexagonal close-packed α modification transforms on heating to the body-centered cubic β -form between 1327 and 1527°C ; DUWEZ⁸ places the transformation temperature at $1310 \pm 10^\circ\text{C}$, DEARDORFF AND KATO¹³ place it at $1750 \pm 20^\circ\text{C}$, while according to FAST⁹ it occurs at $\sim 1950^\circ\text{C}$. Our own investigation places it at approximately 1950° , with the melting point at 2190°C .

Based on a combination of X-ray diffraction patterns and the microscopic examination of the structures of quenched alloys, the body-centered cubic β -Hf phase field was shown to extend from pure Hf to 58.5 at. % hafnium at 1915°C at which temperature the β and hexagonal $\epsilon_1\text{-Mo}_2\text{Hf}$ phases are in equilibrium along a eutectic horizontal. The β -phase also extends down to a eutectoid point at 72 at. % hafnium and 1215°C , at which temperature the β -phase splits up into cubic $\eta\text{-Mo}_2\text{Hf}$ + $\alpha\text{-Hf}$ primary solid-solution, the latter containing about 0.8 molybdenum.

Below 90 at. % hafnium, β -phase alloys are easily retained in the body-centered cubic form on quenching and, as a result, the Mo_2Hf + $\beta\text{Hf}/\beta\text{Hf}$ boundary is easy to determine both micrographically and by X-ray diffraction as is also the portion

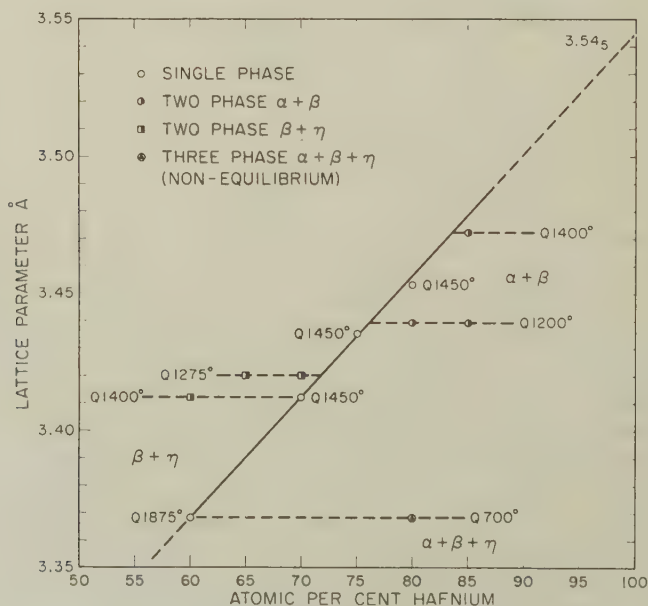


Fig. 3. Room temperature lattice parameters of the b.c.c. β -Hf phase-structure in Mo-Hf alloys retained by quenching (absolute Angstrom units).

of the β -Hf/ α - β boundary to about 90% hafnium. At higher hafnium contents, the β to α transformation becomes progressively more rapid and cannot be completely suppressed above 92.5% hafnium, the process being closely analogous to the marten-

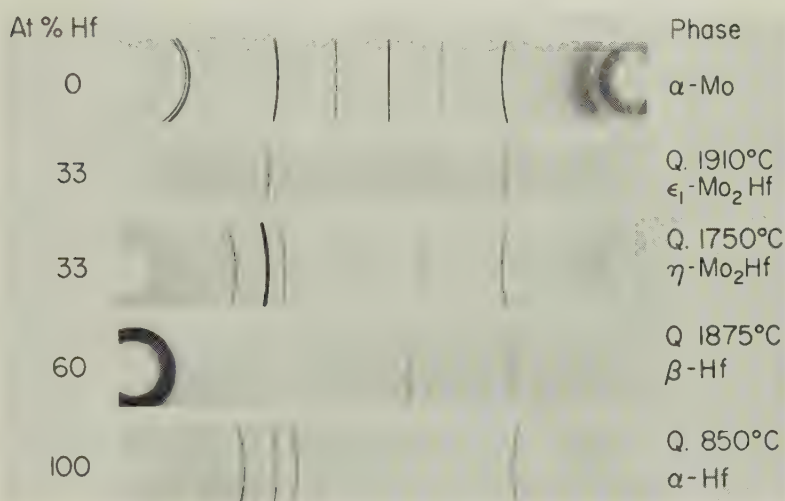


Fig. 4 X-ray diffraction patterns of Mo-Hf alloys.

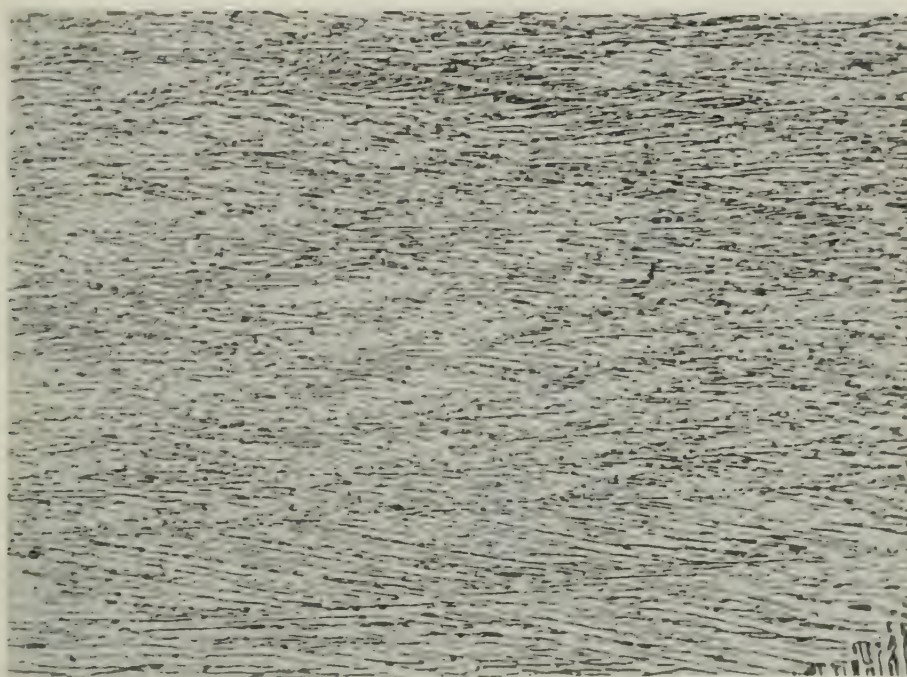


Fig. 5 99.0 at % Hf quenched after lump annealing 15 h at 2050°C. Complete martensitic transformation from the b.c.c. β -form to the hexagonal close-packed α -phase.

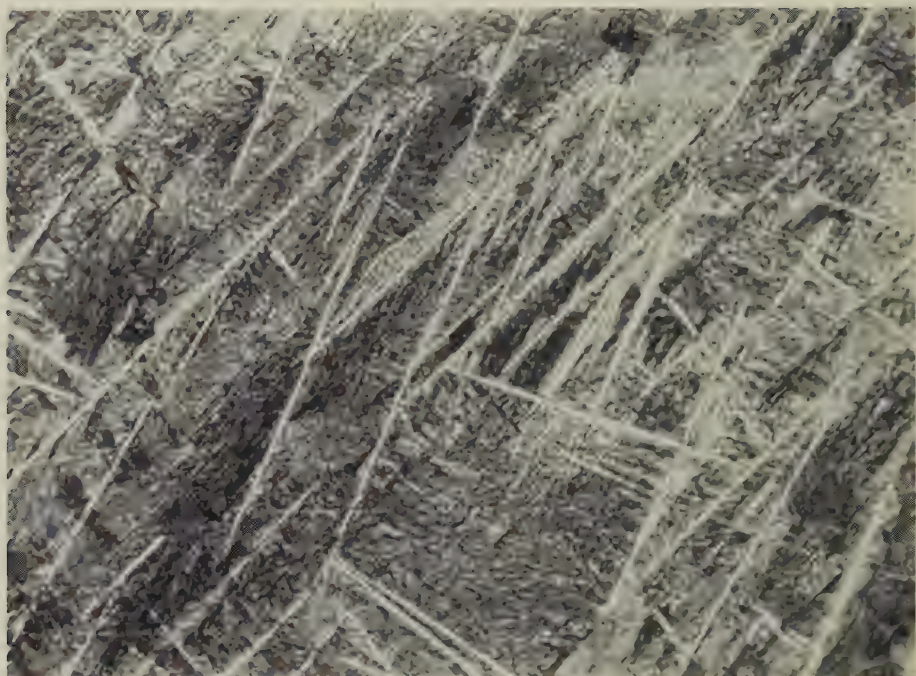


Fig. 6. 99.0 at.% Hf quenched after lump annealing for 30 min at 1900°C. Needles of primary α in background of completely transformed β .

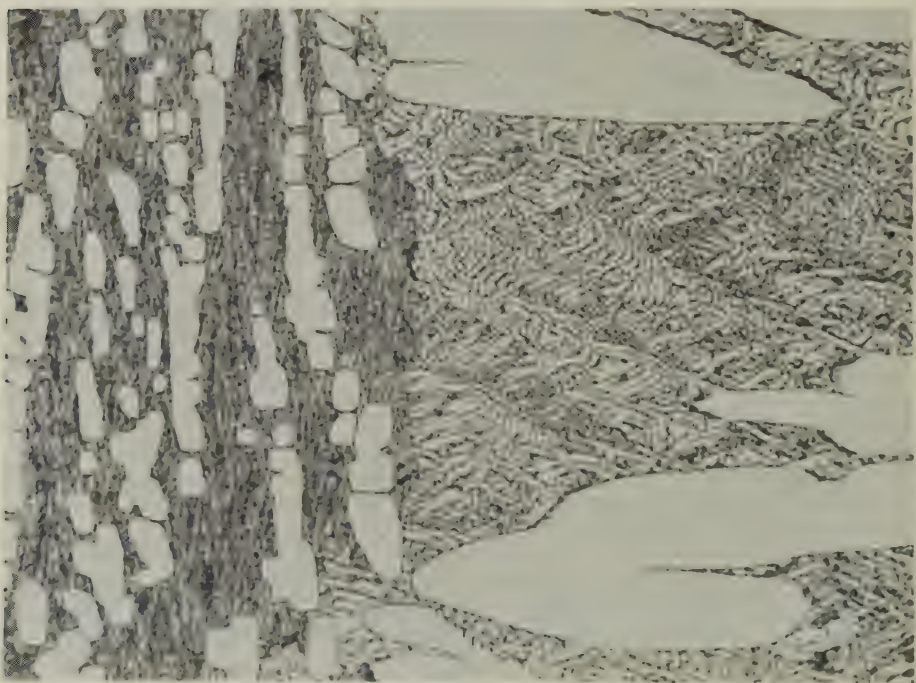


Fig. 7. 99.0 at.% Hf quenched after lump annealing for 3 h at 1880°C. Large slabs of primary α in matrix of completely transformed β .

sitic transformation from the high temperature body-centered β -phase to the hexagonal close-packed α -phase in zirconium¹⁰ and titanium alloys¹¹.

Since it was impossible to effect any stress-relieving anneal on powdered β -phase alloys owing to the instability of the phase, all the X-ray diffraction work was carried out on the cold-worked powders prepared by crushing the as-quenched

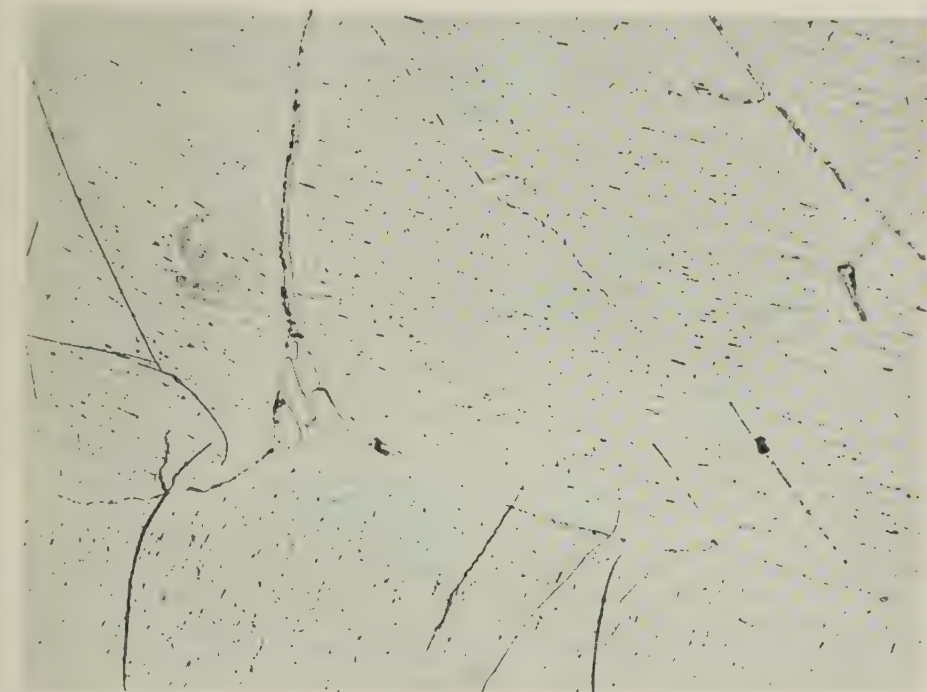


Fig. 8. 99.0 at.% Hf. Alloy lump annealed 16 h at 1950°C, slowly cooled over 24 h to 1200°C, held at 1200°C for 3 days and quenched. Mainly α -phase with particles of η -Mo₂Hf resulting from the eutectoid decomposition $\beta \rightarrow \alpha + \eta$.

lumps. Fortunately, β -phase alloys are relatively brittle and crush to fine powder without undue broadening of the high order reflexions. Lattice parameters of quenched β -phase alloys prepared in this manner are illustrated in Fig. 3, while a typical β -phase powder diagram is shown in Fig. 4 along with those from the other single-phase fields. The curve is remarkably linear and extrapolates to a value of 3.545 Å for the hypothetical room temperature spacing of pure β -hafnium. This value is significantly different from the value of 3.50 Å obtained by DUWEZ¹² by means of a long extrapolation across the niobium-hafnium system, taken from the phase boundary of the body-centered cubic α -Nb phase at 30 at.% hafnium all the way to 100 at.% hafnium.

Contrasted with the great extent of the β -Hf phase field, that of the hexagonal close-packed α -Hf phase is extremely narrow, ranging from approximately 99.2 to 100 at.% hafnium with no appreciable changes in lattice parameters. As we have stated above, it is impossible to suppress completely the transformation from the

β to the α form above 92.5 at. % hafnium. Figs. 5-8 illustrate the changes which take place in the microstructure of an alloy containing 99.0 at. % hafnium after equilibrating and quenching from the respective temperatures 2050, 1900, 1880 and 1200°C. These changes, coupled with similar findings for β -phase alloys confirm FAST in placing the α to β transformation at $\sim 1950^\circ\text{C}$ and place the eutectoid at $\sim 1215^\circ\text{C}$.

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CONSTITUTION STUDIES ON THE NEPTUNIUM-PLUTONIUM
ALLOY SYSTEM

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SUMMARY

Neptunium-plutonium alloys have been examined over the complete range of compositions using thermal analysis, dilatometric and X-ray techniques. The probable form of the constitution diagram has been determined, the most noteworthy feature being the extremely high solubilities of neptunium in the monoclinic α and β phases of plutonium.

An intermediate phase exists at high temperatures at the plutonium-rich end of the system; its crystal structure is complex but an orthorhombic cell has been tentatively assigned to it with $a = 10.86 \text{ \AA}$, $b = 10.67 \text{ \AA}$, $c = 10.43 \text{ \AA}$ for a 19 wt.% neptunium alloy at 375°C . The relation of this cell to the cubic ζ -plutonium-uranium and δ -neptunium-uranium phases is discussed.

γ -neptunium and ϵ -plutonium are completely miscible and by extrapolation of the high temperature lattice parameters a value of $3.518 \text{ \AA}$ was obtained for the γ -neptunium parameter at 500°C . There is appreciable solubility of plutonium in the α and β phases of neptunium, although the exact values are not known. The solidus shows a marked depression in the middle of the system and only varies slowly with composition over a large part of the diagram.

I. INTRODUCTION

The neptunium-plutonium system is the second neptunium alloy system investigated by the present authors; the results of the earlier work on the neptunium-uranium system have already been published¹. The alloying of neptunium with plutonium was the logical continuation of the previous investigations into the systems neptunium-uranium and plutonium-uranium which had certain features in common². The present results are, however, so surprising that the neptunium-plutonium system must be considered as unique among the plutonium alloy systems so far examined.

The plutonium-rich part of the system has also been studied by COPE³, but his results do not agree in detail with those presented here. For reasons discussed in Section 3(b), the present results are thought to give a truer representation of the constitution diagram.

2. EXPERIMENTAL TECHNIQUES

As with the work on the neptunium-uranium system, only some 2-3 g of neptunium were available for the whole study. Various compositions were obtained by repeatedly remelting three initial alloys containing 97, 54 and 10 wt.% neptunium; the plutonium content was increased by 2-3% between each melt, the latter operation being

carried out in a small argon-arc furnace. The process was exactly similar to that described previously¹. The major impurities in the neptunium were 0.34 wt.% calcium and 0.22 wt.% uranium but it is probable that the calcium was removed by volatilisation during the first arc melting process. The plutonium was considerably purer and certainly contained less than 1000 p.p.m. total impurities.

The alloys were examined by thermal analysis, dilatometry and X-ray techniques as in the earlier work with the neptunium-uranium alloys. The high temperature powder camera and room temperature focussing camera previously used were, however, supplemented with a high temperature diffractometer.

For thermal analysis and dilatometry, calibrated chromel-alumel couples were used throughout since the maximum phase transition temperature encountered in the system was the melting point of pure plutonium, 639°C. The solidus-liquidus interval was small for all compositions and it was therefore possible to determine both points on any alloy without keeping the material molten or semi-molten in the crucible for any length of time; this allowed more frequent determinations to be made of the liquidus temperature than had been possible with neptunium-uranium alloys since in the present instance there was less danger of reaction between the liquid alloys and the alumina crucibles. However, a slight discontinuity in the solidus at one point may have indicated some contamination to have occurred in the present work (see Section 3(d)).

3. RESULTS

The thermal analysis and dilatometric results outlined the form of the diagram as shown in Fig. 1. X-ray data confirmed the results and gave further information on

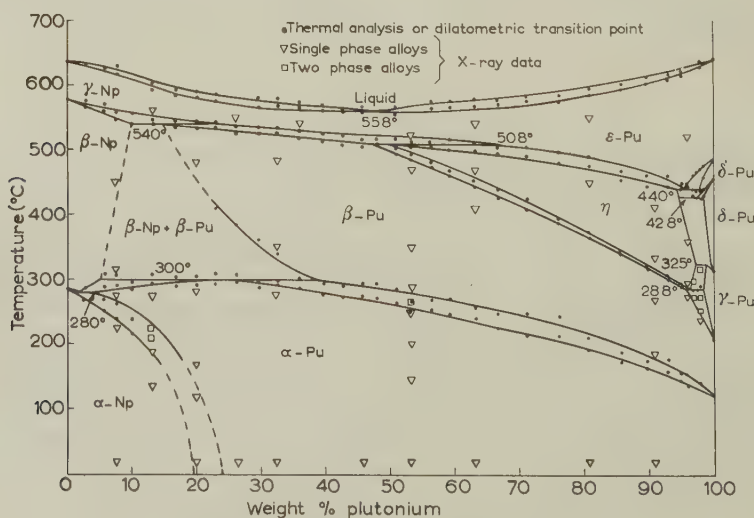


Fig. 1. The neptunium-plutonium constitution diagram.

the boundaries of the single phase fields; for the sake of clarity, these have been largely omitted from Fig. 1 and are shown instead on Figs. 2 and 3, which are enlargements of the neptunium-rich and plutonium-rich ends of the system respectively.

The quoted transition temperatures are those obtained on heating at rates of about $1^\circ\text{C}/\text{min}$ except for liquidus values which were taken on cooling. Though by normal metallurgical standards, these rates should be slow enough to approximate to equilibrium rates, the work of HILL⁴ has shown that the values may err considerably on the high side for the lower temperature plutonium transitions.

(a) *The α -plutonium field*

Neptunium is extremely soluble in α -plutonium and it is probable that only the difference in crystal structures of α -neptunium and α -plutonium prevents complete solid solubility occurring. At room temperature, the maximum solubility of neptunium

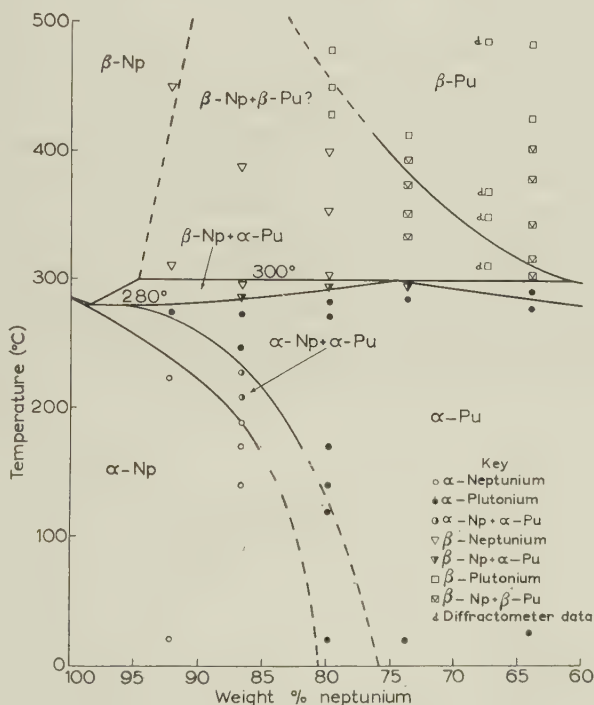


Fig. 2. X-Ray data, neptunium-rich alloys.

is in the range 75–80 wt.% and this increases with temperature until it reaches about 96 wt.% at 275°C . The exact value for the boundary at room temperature is uncertain since it appears to steepen rather suddenly at temperatures below 200°C (Figs. 1 and 2). An 80% neptunium alloy gave a single phase α -plutonium pattern even after immersing the filings in liquid nitrogen, whilst an 87% neptunium alloy was single phase α -neptunium up to 190°C . Without a rather sudden change in the slope of the appropriate boundaries, these results are difficult to reconcile.

It was generally thought that the maximum temperature to which α -plutonium was stable represented a congruent transformation point to β -neptunium, but for reasons discussed in Section 3(b), it is now believed that the α -phase decomposes peritectoidally by the reaction $\alpha\text{-Pu} \rightarrow \beta\text{-Np} + \beta\text{-Pu}$ at $300 \pm 5^\circ\text{C}$.

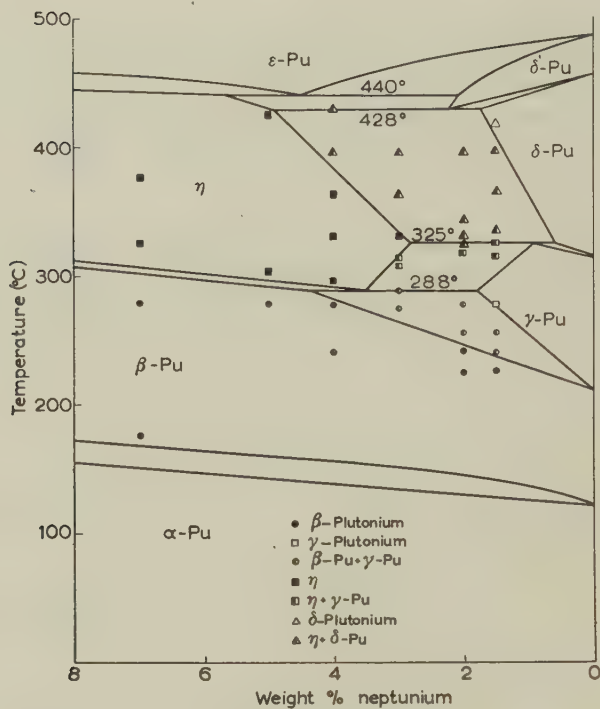
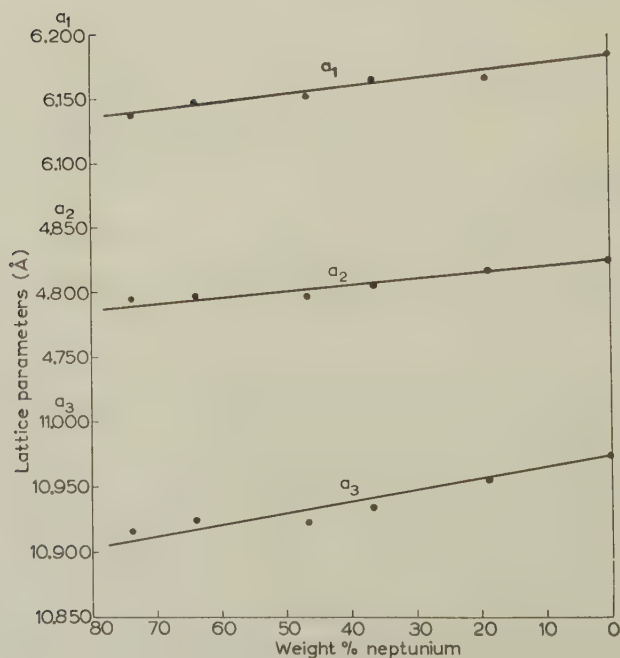


Fig. 3. X-Ray data, plutonium-rich alloys.

Fig. 4. Lattice parameter-composition curves, α -plutonium field (20°C).

The lattice parameters of α -plutonium decrease steadily with increasing neptunium content, the maximum contraction being slightly less than 1% in each of the parameters (Fig. 4); the angle β of the monoclinic cell remains essentially constant. Thus even though the neptunium atoms are some 1% lighter than the plutonium atoms, there is an overall increase in density to a maximum of 20.1 g/cm³.

For alloys containing about 50% neptunium, dilatometric and electrical resistivity measurements suggested that a phase boundary was crossed at temperatures between 100° and 200°C. X-ray examinations failed to show any change of structure across this apparent boundary and it was concluded that this was probably a second order phase change; no further work has been carried out on this problem.

(b) *The β -plutonium field*

Neptunium is highly soluble in β -plutonium, the maximum value being approximately 85% at a temperature of 540°C where a peritectoid reaction, $\beta\text{-Pu} \rightarrow \beta\text{-Np} + \gamma\text{-Np}$ occurs. The temperature range of the β -plutonium field is considerably increased by neptunium additions and for alloys in the 50/50 region reaches over 200°C. The boundary between the β -plutonium and β -plutonium + β -neptunium fields is extremely uncertain, the behaviour of the alloys on X-ray examination being very variable; thus the high temperature diffractometer tended to show alloys as single phase β -plutonium when the high temperature powder camera showed adjacent alloys to be largely β -neptunium with only a trace of β -plutonium, until about 400°C, above which temperature the pattern became that of β -plutonium. The results suggest that the free energy-composition curves for β -neptunium and β -plutonium must be very close in this part of the diagram, and that traces of contaminants,

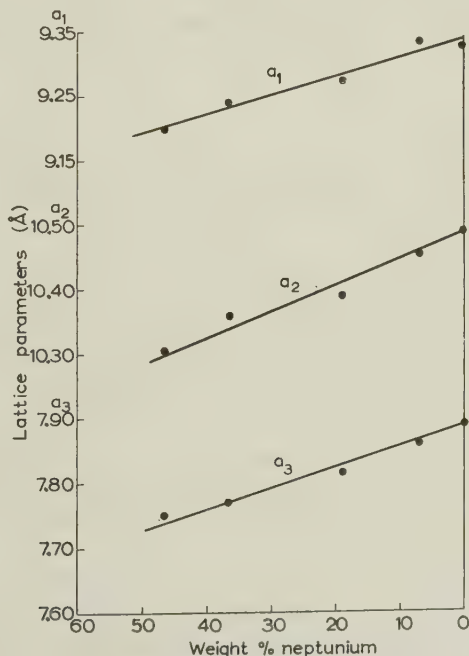


Fig. 5. Lattice parameter-composition curves, β -plutonium field (290°C).

such as silicon or oxygen from the powder camera capillaries may cause a transformation from one phase to the other. The equilibrium structure for this region has been assumed to be β -neptunium + β -plutonium, which would imply that α -plutonium decomposes by a peritectoid reaction on heating; the thermal analysis results are in general accordance with this view and in addition, for alloys containing 65–80 wt. % neptunium, gave some indications of a possible β -Pu/ β -Pu + β -Np boundary.

The lattice parameters of β -plutonium behave similarly to those of α -plutonium, *i.e.* decrease with increasing neptunium content, although the rate of decrease is considerably greater and apparently varies more between the individual parameters (Fig. 5). Due to the complexity of the structure, unambiguous indexing of the higher angle lines of the diffraction patterns proved impossible and the consequent need to use low angle lines severely limited the accuracy with which the lattice parameters could be determined; for plutonium-rich alloys, examination had to be carried out at lower temperatures than for the higher neptunium content alloys because of the shape of the field — the parameters were then adjusted to the higher temperatures using the expansion coefficients for pure plutonium⁵. With neptunium-rich alloys, oxidation proved a serious handicap at the relatively high temperature range of existence of the phase and no attempt was made to determine the lattice parameters from the reduced number of visible lines.

Work by COPE³ indicated a much more restricted solubility of neptunium in β -plutonium and the existence of a second intermetallic phase in this part of the diagram. However, the existence of this phase and the low solubility limit for the β -plutonium field were inferred from dilatometric and thermal analysis data, no direct X-ray observations being made. Since unambiguous single phase β -plutonium patterns have been obtained by the present authors in this region, both with the diffractometer and with the high temperature powder camera, the form of the diagram presented here is thought to be more probably correct.

(c) *The γ -, δ - and δ' -plutonium fields*

Solubility of neptunium is highly restricted in these phases, the maximum value being of the order of 2% in each phase (Fig. 3). The low solubilities are associated with the presence of the intermetallic η phase and a correlation exists with the equivalent region of the plutonium–uranium system².

The peritectoid reaction γ -Pu $\rightleftharpoons$ η + δ -Pu could not be detected on thermal analysis but was shown to occur at 325°C by X-ray examination. The temperature of the reaction was determined to only $\pm 5^\circ\text{C}$ but even allowing for calibration errors in the temperature measurements this was sufficient to show that the reaction was a peritectoid and not the alternative eutectoid reaction δ -Pu $\rightleftharpoons$ η + γ -Pu. Dilatometry confirmed this by indicating that in a 1.5% neptunium alloy the $\gamma/\gamma + \eta$ boundary was at a sufficiently high temperature to preclude the possibility of a eutectoid reaction. The δ -prime phase decomposes eutectoidally into η and δ -plutonium at 428°C.

(d) *The ϵ -plutonium field*

Complete solid solubility exists between ϵ -plutonium and γ -neptunium. X-ray examination at temperatures close to the solidus has shown only the lines of a body-centred cubic phase plus those due to the various oxides. At the neptunium-rich

end of the system, some difficulty was experienced because of the unfortunate overlapping of the lines of the oxide (Np, Pu)O and of γ -neptunium as first noted by ZACHARIASEN⁶, but as the plutonium content was raised the lines gradually separated and for alloys containing more than 30% plutonium the patterns were quite distinct. It was not possible to take all the photographs at the same temperature but the values of the lattice parameter for the different alloys were all adjusted to a temperature of 550°C, assuming the linear expansion coefficient to be independent of composition and therefore equal to that of ϵ -plutonium, namely $36.5 \cdot 10^{-6}/^{\circ}\text{C}$. In the case of data obtained from the powder camera, a Nelson-Riley extrapolation was applied to determine the best value of the lattice parameter whilst for the diffractometer results, a simple average was used. The resultant lattice parameter-composition curve is shown in Fig. 6; visual extrapolation to pure neptunium gives a parameter of 3.513 Å, whilst a least-square fitting of the points gives a corresponding value of 3.511 Å.

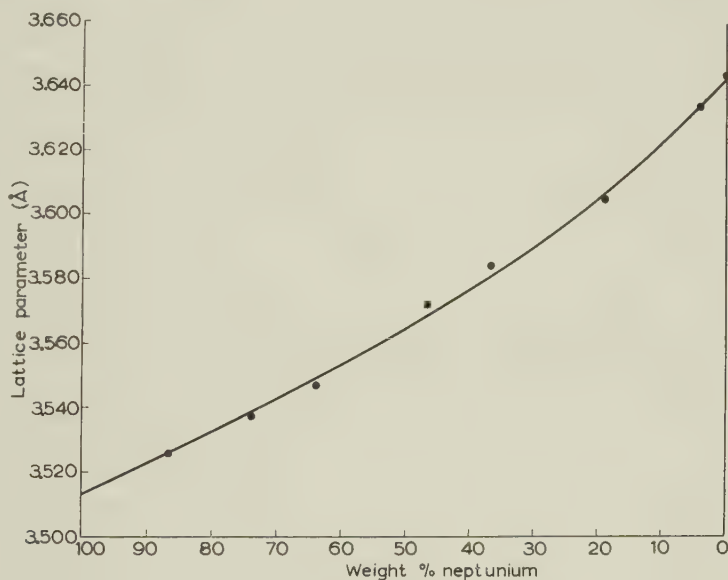


Fig. 6. Lattice parameter-composition curves, ϵ -Pu $\equiv$ γ -Np field (550°C).

Since γ -neptunium is not a stable phase at 550°C, this value has been adjusted to a higher temperature, again assuming a value of $36.5 \cdot 10^{-6}/^{\circ}\text{C}$ for the coefficient of linear expansion; at 600°C the resultant lattice parameter is 3.518 Å, in good agreement with ZACHARIASEN's approximate value of 3.52 Å.⁶ At the plutonium-rich end of the system the ϵ phase containing 4 wt.% neptunium decomposes by a eutectoid reaction $\epsilon\text{-Pu} \rightleftharpoons \eta + \delta'\text{-Pu}$ at 440°C.

The solidus-liquidus curves pass through a shallow depression in the middle of the system and in view of the X-ray data presumably touch at some minimum temperature, although this point was not detected by thermal analysis. A small discontinuity was observed at the composition where the originally neptunium-rich alloy met the 50/50 alloy; this suggested that the neptunium-rich alloy had become slightly contaminated with some impurity which depressed the solidus but no corresponding discontinuities were observed on the solid state transitions at this composition.

(e) *The η phase*

This intermetallic phase extends 50–3 wt. % neptunium, being formed by a peritectoid reaction, $\beta\text{-Pu} + \epsilon\text{-Pu} \rightleftharpoons \eta$, at 508°C and decomposing by the eutectoid reaction, $\eta \rightleftharpoons \beta\text{-Pu} + \gamma\text{-Pu}$ at 288°C. X-ray examination of the phase gave a pattern of many lines, comparable in complexity to that of β -plutonium. Attempts to index the lines by the standard techniques failed and comparison with the lines shown by ζ - and η -plutonium–uranium⁸ showed that the material was not iso-structural with either of these phases. It was noted, however, that the line intensities at low angles exhibited some correlation with those of the ζ -plutonium–uranium structure, suggesting that the η -neptunium–plutonium lattice was related to the cubic ζ structure. On this basis, it proved possible to index the lines on an orthorhombic distortion of the ζ cell, with only small differences in magnitude between the three parameters. Table I gives the results for a 19 wt. % neptunium alloy at 375°C; the lines due to (Np, Pu)O and (Np, Pu)O₂ have been omitted as have also a few extremely weak lines at low angles. It is also possible that some of the very weak lines at higher angles do not actually exist, since they were not always observed on films taken at different temperatures.

TABLE I
OBSERVED AND CALCULATED REFLECTIONS, η PHASE (19 wt. % Np, 375°C)
Calculated unit cell, $a = 10.86 \text{ \AA}$, $b = 10.67 \text{ \AA}$ and $c = 10.43 \text{ \AA}$

Indices	Observed lattice spacing, $1/A$	Intensity	$1/d^2$ obs.	$1/d^2$ calc.
410	2.629	S	0.1447	0.1445
401				0.1449
004	2.607	S	0.1471	0.1472
322	2.600	S	0.1479	0.1482
223	2.569	MS	0.1515	0.1518
330	2.538	MS	0.1552	0.1553
303	2.507 ₆	S	0.1591	0.1591
331	2.460 ₅	MW	0.1651	0.1645
313	2.443 ₅	W	0.1675	0.1679
133	2.425	VW	0.1700	0.1703
240	2.398	VW	0.1739	0.1744
042	2.378	W	0.1768	0.1773
421	2.348	VW	0.1814	0.1800
204				0.1811
412				0.1823
233	2.251	VW	0.1974	0.1957
422	2.199	W	0.2068	0.2076
430	2.165	VW	0.2133	0.2147
043	2.120	VW	0.2225	0.2233
035	1.7997	VW	0.3087	0.3090
352	1.7338	W	0.3327	0.3326
162	1.6664	VW	0.3601	0.3614
444	1.5363	VW	0.4237	0.4234
070	1.5258	W	0.4295	0.4302
711	1.5181	W	0.4339	0.4335
171	1.4955	MW	0.4471	0.4479
007	1.4882	W	0.4515	0.4508
641	1.4826	W	0.4549	0.4550

The η phase was studied mainly with the high temperature diffractometer --- this had two major advantages over the powder camera in that no absorption correction was necessary and that the diffractometer partially resolved close doublets such as 004 and 322 which appeared as a single line on the powder photographs.

Accurate determinations of the lattice parameters were not possible because of the absence of high angle lines, which in any event would have proved very difficult to index unambiguously. Thus although the phase was studied at different compositions and temperatures, it was not possible to determine either the expansion coefficients or the variation of parameters with composition accurately. For the 19 wt. % neptunium alloy the expansion coefficient appeared to be in the range $25 \pm 5 \cdot 10^{-6}/^{\circ}\text{C}$ for each of the orthogonal directions, whilst increase of plutonium content produced an increase in the lattice parameters. Neither variation of temperature nor composition produced any significant change in the ratios $a : b : c$, indicating that the phase would not revert to the cubic ζ -plutonium-uranium structure at any temperature or composition.

Dilatometric measurements on the 19 wt. % neptunium alloy indicated that the density of the material was some 5.5% below the theoretical X-ray density in both the α and β phase fields, presumably due to the presence of voids. Applying this correction to the observed density in the η field gave a density of 17.56 g/cm^3 at 450°C which would correspond to 53.9, *i.e.* 54 atoms per unit cell. This suggests that the structure consists basically of 27 body-centred cubic ϵ -plutonium cells stacked in a $3 \times 3 \times 3$ arrangement.

(f) The α - and β -neptunium fields

The solubility of plutonium in α -neptunium increases as the temperature is lowered. As discussed in Section 3(a), the maximum solubility is difficult to determine because of the rapid increase in the slope of the $\alpha\text{-Np}/\alpha\text{-Np} + \alpha\text{-Pu}$ boundary as the temperature falls. The probable limit of solubility at room temperature is somewhat less than 20% plutonium.

The extent of the β -neptunium solid solution is even less certain because of the variable behaviour on X-ray examination as described in Section 3(b). It is apparent from thermal analysis that approximately 10% of plutonium is soluble at the β -plutonium peritectoid temperature (540°C) and the form of the α -plutonium peritectoid reaction suggests that the solubility is somewhat lower at 300°C . Below the latter temperature, the phase decomposes by the eutectoid reaction $\beta\text{-Np} \rightleftharpoons \alpha\text{-Np} + \alpha\text{-Pu}$ at about 280°C .

4. DISCUSSION

It is believed that the constitution diagram as drawn in Fig. 1 is correct with the possible exception of the extent of the β -neptunium and β -plutonium fields where, as explained previously, very variable results are obtained. To resolve this difficulty, a technique would be required which would be less dependent on the condition of the specimens surface than is the case with X-ray diffraction methods. Dilatometric and electrical resistivity measurements on comparatively massive specimens would probably be satisfactory but the shortage of neptunium metal precludes the use of such techniques at the present time.

Of the established results, the most noteworthy are the complete solid solubility

between ϵ -plutonium and γ -neptunium, the existence of the η phase and the extremely high solubility of neptunium in the monoclinic α and β phases of plutonium.

In a previous paper on the neptunium-uranium alloy diagram¹ two of the present authors pointed out that although complete solid solubility almost certainly occurred between γ -uranium and γ -neptunium, it has not been possible to verify this by X-ray examination, and the results for the neptunium-plutonium system would be required before it could be definitely stated that the structure of γ -neptunium was body-centred cubic. In the present work, because of the lower temperature range for the γ -Np $\equiv$ ϵ -Pu field as compared with the γ -Np $\equiv$ γ -U field, it has proved possible to obtain X-ray data on the solid solution; oxidation, although serious, no longer completely obscures the lines of the metal phase as in the neptunium-uranium alloys. The cell side for γ -neptunium as obtained by extrapolation of the X-ray data is in excellent agreement with ZACHARIASEN's postulated value and there is now no reason to doubt that the structure of γ -neptunium is indeed body-centred cubic.

The proposed orthorhombic structure for the η phase must be regarded as tentative in view of the large size of the unit cell, but some weight is added to the proposed structure by its relation to the isostructural cubic phases ζ -plutonium-uranium and δ -neptunium-uranium and to the tetragonal η -plutonium-uranium. The interrelation between the phases is unusual in that they have all approximately the same volume for the unit cell but have widely differing densities, thus implying that they contain different numbers of atoms in the unit cell, the respective figures being 58 for the ζ and δ phases, 52 for η -plutonium-uranium and 54 for η -neptunium-plutonium. Since the ζ phase apparently becomes tetragonal at high temperatures, the transition from ζ to η in the plutonium-uranium system involves virtually no change in lattice parameters but the rejection of 6 atoms from the unit cell. The factors governing the composition ranges for these phases are not clear; if ZACHARIASEN's postulated valencies for the various phases of uranium, neptunium and plutonium are adopted, then the electron/atom ratio for the various intermetallic phase fields are different, whether one uses the valencies for the body-centred cubic phases or for the room temperature phases. As the positions of the atoms in the unit cells are not known, it is not possible to state whether geometrical stacking factors are responsible for the existence of these structures.

The extremely high solubility of neptunium in both the α and β phases of plutonium is unique amongst the known plutonium alloy systems. The mutual solubilities of uranium, neptunium and plutonium in the binary systems are shown in Table II.

TABLE II
MAXIMUM MUTUAL SOLUBILITIES OF ACTINIDE ELEMENTS

Solvent	Solute		
	U (%)	Np (%)	Pu (%)
α -U	—	43	15
α -Np	20	—	19
α -Pu	1	96	—
β -U	—	26	20
β -Np	26	—	10
β -Pu	2	86	—

The high solubility of neptunium in the low temperature modifications of each of its neighbouring actinides is very noticeable. No other element is known to dissolve in the lower temperature allotropes of these metals to anything approaching these values; this emphasises that the ability to form the highly directional bonds characteristic of these structures is the main requirement for high solubility. A comparison of the angles between the short bonds in the known structures of uranium, neptunium and plutonium is made in Table III. Since there are 8 distinct atomic positions in the

TABLE III
COMPARISON OF BOND ANGLES FOR SHORT BONDS
IN URANIUM, NEPTUNIUM AND PLUTONIUM

The numbers of bond angles are normalised to a total of about 48 for comparison. In α -neptunium, α -plutonium and γ -plutonium some of the values are averaged over 1–2 degrees.

α -U		α -Np		β -Np		γ -Pu		α -Pu		γ -Pu		δ -Pu		ϵ -Pu	
No.	Angle	No.	Angle	No.	Angle	No.	Angle	No.	Angle	No.	Angle	No.	Angle	No.	Angle
										6	57				
										4	61	16	60		
										2	66				
						24	70½			8	74			24	70½
		4	79	16	78			10	79						
		8	84½					8	84						
32	90	16	90												
				16	102							8	90		
						24	109½	12	113					24	109½
		8	116					2	118	4	119	16	120		
								4	122	8	123				
8	127	8	127	16	125			6	127						
								3	>140	2	150				
8	180	4	180			8	180			3	180	4	180	8	180

α -plutonium unit cell, the other values have been scaled up so that approximately equivalent total numbers of bond angles may be compared. Due to the singular nature of 2 of the atomic positions in the α -plutonium cell, there are only 45 short bonds for the 8 atoms as compared with 48 such bonds in the α -neptunium and α -uranium structures.

A noteworthy feature is the predominance of 90° bond angles in α -uranium compared with half as many such angles in α -neptunium and their complete absence in α -plutonium. α -neptunium clearly represents an intermediate stage between α -uranium and α -plutonium since it shows features in common with each of the structures and this may explain the high solubility of neptunium in both.

The low solubility of neptunium in γ - and δ -plutonium is rather surprising in view of the high solubilities in the more complex α - and β -plutonium phases. This low solubility can be attributed either to a bonding effect or to the interference of the η phase which must then be assumed to be of relatively high stability.

In both α - and β -neptunium⁵ each atom has 4 neighbours much closer than the others, forming apparently strongly directed covalent bonds with the angles between them not less than 78° (Table III). In γ - and δ -plutonium the bonding is presumably

of a more metallic and less directional character, but both phases have a high proportion of bond angles in the range $57\text{--}66^\circ$ and at these temperatures neptunium may not be able to form such low angle bonds.

ZACHARIASEN has drawn attention⁵ to the close relationship of α - and β -neptunium to the body-centred cubic structure. It was mentioned above (Section 3(e)) that the η unit cell probably comprises a distorted packing of 27 body-centred cubic ε -cells. Hence it may be that the neptunium atom is at its most stable in a body-centred cubic-like structure, thus giving a low free energy to the η phase. This will of course help to limit the solubility of neptunium in γ - and δ -plutonium, particularly if the bond angle effect reduces the stability of the solution in these phases.

The alloying behaviour of neptunium with thorium should be of considerable interest; thorium is the only other actinide element at present available in sufficient quantities to allow the use of conventional physico-metallurgical techniques. It also represents an unusual case in that its behaviour with uranium differs widely from that with plutonium, highly restricted solubility in α -thorium occurring with the former and extensive solubility with the latter^{10,11}. Another element which might indicate whether neptunium is closer metallurgically to plutonium than to uranium, or *vice versa*, is zirconium^{10,12}, marked differences again occurring in the binary systems at low temperatures. This however may be due in part to the existence of a face-centred cubic modification in plutonium but not in uranium; since neptunium does not exhibit such a structure and in terms of numbers of phases and complexity of crystal structure superficially resembles uranium rather than plutonium, it may be anticipated that its general alloying behaviour will be closer to that of uranium than to that of plutonium.

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PRÉPARATION DE TÉTRAFLUORURE DE TITANE À PARTIR D'UN MINÉRAI TITANIFÈRE PAUVRE

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RÉSUMÉ

Après un examen des inconvénients des méthodes classiques, et spécialement dans le cas du traitement de minerais à basse teneur, on propose un procédé comprenant les trois stades suivants:

- (1) enrichissement magnétique de 20 à 50% de bioxyde de titane;
- (2) réduction sélective par l'hydrogène donnant un mélange de fer et de bioxyde de titane;
- (3) Fluoruration sélective par le fluorure d'hydrogène anhydre, de manière à produire du tétrafluorure de titane volatil et un résidu constitué d'un mélange de fer, oxydes de fer et fluorures de fer.

SUMMARY

After reviewing the drawbacks of the conventional processes, especially when applied to low grade ores, a three-step procedure is proposed consisting of:

- (1) magnetic enrichment of 20 to 50% titanium dioxide;
- (2) selective hydrogen reduction producing a mixture of iron and titanium dioxide;
- (3) selective fluorination with anhydrous hydrogen fluoride, giving volatile titanium tetrafluoride and a residue consisting of a mixture of iron, iron oxides and iron fluorides.

INTRODUCTION

Au cours des dernières années, la demande en titane métallique suscitée par les impératifs militaires a subi des modifications rapides en sens divers. La tendance du marché n'est guère prometteuse pour le producteur, du moins dans l'immédiat. Parallèlement à ces fluctuations, il existe heureusement un accroissement lent mais continu de la consommation de titane dans diverses branches de l'économie et en particulier dans l'industrie chimique. Bien que les gisements riches actuellement exploités suffisent amplement à couvrir les besoins de la jeune industrie du titane métallique et de son aînée produisant l'oxyde pour pigment (cette dernière restant toujours la plus importante par les tonnages en jeu), il est cependant de bonne politique de prévoir dès maintenant la valorisation des minerais à basse teneur afin de pouvoir répondre à l'accroissement futur de la consommation de l'économie civile. Une autre raison, qui milite dans le même sens, est l'étroite localisation géographique

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des minerais riches qui contraste avec la distribution dispersée des gîtes pauvres économiquement inexploitable pour l'instant.

Il semble donc opportun de consacrer les efforts nécessaires à la mise au point du traitement des minerais titanifères à basse teneur par un procédé n'exigeant pas de dépenses prohibitives en réactifs, en énergie et en appareillage, afin de pouvoir utiliser ces minerais pauvres au moment voulu. C'est le but du présent travail.

Il est commode de classer les gîtes titanifères en trois catégories:

(1) les gisements de sables titanifères, dont on peut extraire aisément des concentrés de rutile (TiO_2) ou d'ilménite (FeTiO_3) par les méthodes classiques de préparation des minerais;

(2) les gîtes d'ilménite riche (35 à 50% TiO_2) formés de roches en place;

(3) les dépôts de titanomagnétite à faible teneur (15 à 25% TiO_2), la titanomagnétite étant un mélange intime de magnétite (Fe_3O_4) et d'ulvospinel (FeTiO_4), tous deux fortement paramagnétiques, avec l'ilménite qui est légèrement paramagnétique.

C'est ce dernier type de gisement qui contient les réserves potentielles les plus importantes, mais qui sont inexploitées et inexploitable pour l'instant.

Le premier objet de la présente étude consistait à rechercher les moyens d'enrichir ces minerais à basse teneur afin de permettre leur traitement par un des procédés connus, déjà en usage pour les minerais des deux premiers types.

Dans le cas du minerai pauvre étudié, on a constaté qu'une partie importante de l'oxyde de titane pouvait être récupérée par concentration magnétique. Les résultats de cette recherche ne seront cependant pas détaillés dans cet article.

Mais le but principal de ce travail consistait à rechercher un procédé plus efficace que les procédés classiques, après avoir examiné ceux-ci d'une manière critique. Il convient à ce propos de signaler que les procédés existants comportent généralement deux stades:

(1) réduction à haute température produisant une fonte et une scorie titanifère contenant encore des quantités notables de fer;

(2) séparation d'un bioxyde de titane utilisable et des impuretés de la scorie (oxyde de fer principalement).

Dans le cas de minerais à très haute teneur en titane, le premier stade peut être omis; quand il s'avère nécessaire, il peut s'effectuer aisément suivant le mode opératoire mis au point par le Bureau of Mines Canadien; c'est pourquoi cette étape du traitement n'a pas été envisagée dans la présente étude, qui a donc été consacrée aux améliorations à apporter au second stade.

Ce dernier est généralement réalisé par l'une ou l'autre des méthodes suivantes:

(1) lixiviation sélective du produit titanifère par un acide, de manière à obtenir un résidu de TiO_2 et une solution de sels de fer;

(2) chloruration du produit titanifère, avec ou sans réduction préalable, suivie de la séparation par voie physique des chlorures de fer et de titane formés.

Les principaux inconvénients de ces procédés sont:

(1) pour le premier: production de grandes quantités de sels de fer (généralement du sulfate), difficiles à vendre ou à valoriser d'une manière économique;

(2) pour le second: difficultés techniques provoquées par des corrosions et des bouchages de tuyauteries, ainsi que production de grandes quantités de chlorure ferrique pour lesquelles il n'existe pas de débouché adéquat.

Malgré ses désavantages, le premier procédé est couramment utilisé dans la fabri-

cation du blanc de titane, car il fournit le titane sous forme d'oxyde comme le requiert cette industrie; il ne sera donc pas examiné davantage dans cette étude.

D'autre part, la production de titane métallique nécessite comme matière première un tétrahalogénure de titane, produit généralement par le procédé de chloruration.

Comme les chlorures de fer et de titane sont malheureusement tous deux volatils et présentent peu de différence entre leurs points d'ébullition (TiCl_4 , 136.4°C ; FeCl_3 , 315°C), leur séparation n'est pas sans offrir de grandes difficultés. En outre, on se trouve devant la nécessité de s'assurer un débouché pour des quantités de chlorure ferrique proportionnelles à la production du composé titanifère. C'est pourquoi, on a envisagé de produire plutôt d'autres halogénures, plus faciles à séparer que les chlorures.

Des essais préliminaires de bromuration et d'ioduration ont été effectués, mais ne seront pas décrits, car leur intérêt pratique est restreint, sinon nul.

Par contre, on a constaté qu'un procédé de fluoruration donnait la possibilité de séparer aisément le fer du titane, grâce à la grande différence de volatilité des fluorures de fer et de titane (TiF_4 bout à 284°C ; FeF_3 et FeF_2 se décomposent à haute température); un autre avantage de ce procédé est qu'il ne requiert pas une consommation excessive de produits chimiques coûteux.

FLUORURATION PAR LE FLUORURE D'HYDROGÈNE GAZEUX

Plan des recherches

Avant d'étudier l'action de HF sur les minerais de titane, enrichis éventuellement par concentration magnétique, on a effectué des essais préliminaires de fluoruration des oxydes simples de fer et de titane; on a examiné dans chaque cas l'influence de la température, du débit de gaz et de la composition du mélange gazeux. On a recherché également l'action favorable que pourrait exercer une réduction préalable des minerais de titane par l'hydrogène.

Appareillage

Après quelques essais d'orientation où NH_4FHF a servi comme agent fluorant, on a utilisé exclusivement le fluorure d'hydrogène, pur ou en mélange avec d'autres gaz, dans l'appareil représenté Fig. 1.

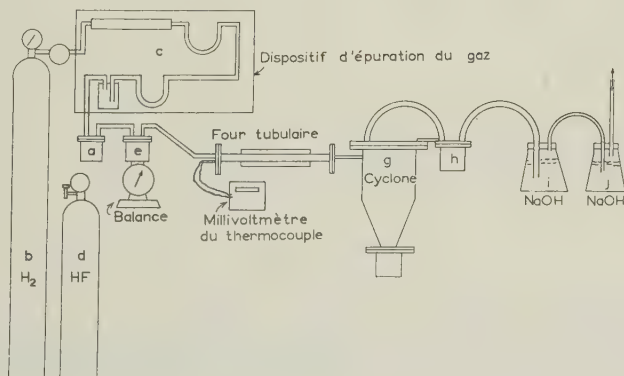


Fig. 1. L'appareil pour fluoruration par HF gazeux.

Le four de fluoruration *f* est alimenté en fluorure d'hydrogène par le réservoir *e*; on remplit ce réservoir au préalable en le raccordant à une bonbonne de HF liquide au moyen d'un tuyau souple en téflon avec gaine tressée en acier inoxydable.

Par suite du bas point d'ébullition de HF (19°C sous pression normale), il est possible de condenser ce gaz dans le réservoir *e*, à condition que ce dernier soit refroidi dans un bain de glace fondante; par pesée continue du réservoir *e*, il est possible de déterminer l'instant où le remplissage est achevé et de mesurer de même le taux de consommation de HF pendant l'essai proprement dit.

L'échantillon d'oxyde, d'un poids de 20 g environ, est placé dans une nacelle de graphite qui est introduite dans le four de fluoruration; ce four est construit en inconel et est pourvu de joints en téflon, comme le représente la Fig. 2.

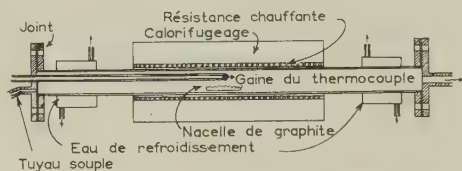


Fig. 2. Four de fluoruration.

Un débit de fluorure d'hydrogène est engendré, soit par réchauffage du réservoir *e*, soit par balayage de celui-ci par un autre gaz (argon ou hydrogène); après avoir traversé le four de fluoruration, les gaz passent dans un condenseur-cyclone, où les fluorures métalliques se séparent, puis dans un flacon de garde et deux barboteurs contenant une solution de soude caustique.

Mode opératoire

Quand l'échantillon d'oxyde est en place, le four de fluoruration est chauffé jusqu'à la température de réaction sous un courant d'argon. Le mélange gazeux fluorant est alors introduit sous débit contrôlé et avec une composition bien déterminée; la durée de la fluoruration est accrue d'un essai à l'autre, jusqu'à ce qu'un allongement supplémentaire du temps de fluoruration soit sans influence sur les résultats. Après les essais, les résidus contenus dans la nacelle et les condensats sont enlevés, pesés et analysés.

Matières premières

Les matières premières utilisées sont: TiO_2 ($D = 79 \mu$); Fe_2O_3 ($D = 43 \mu$); ilménite ($D = 7 \mu$); ilménite réduite ($D = 7 \mu$).

Les diamètres D indiqués sont les diamètres moyens des grains des poudres, mesurés suivant la méthode de MARTIN et obtenus par la relation

$$D = \frac{\sum_i n_i x_i^3}{\sum_i n_i x_i^2}$$

où n_i est le nombre de grains de diamètre x_i , comptés sur une microphotographie. Dans la mesure du possible, ces déterminations statistiques ont été vérifiées par tamisage sur tamis de la série Tyler.

Résultats des essais de fluoruration de TiO_2

Les pertes en TiO_2 des échantillons sont indiquées au Tableau I.

Ce tableau montre que les taux de fluoruration sont fortement influencés par la composition du gaz; quand l'agent fluorant est du HF pur ou mélangé à l'argon, les résultats sont nettement insuffisants; la présence d'une certaine quantité d'hydrogène

TABLEAU I
PERTE EN TiO_2 DES ÉCHANTILLONS (% DU POIDS INITIAL DE TiO_2)

Température	Débit de HF (g/h)	Composition du mélange gazeux (% vol.)				
		20% HF + 80% A	50% HF + 50% A	100% HF	80% HF + 20% H_2	90% HF + 10% H_2
400	15	—	—	1	20	21
	30	2	3	4	25	24
	50	3	5	8	28	26
480	15	5	10	19	59	57
	30	8	14	26	27	72
	50	13	15	30	79	73
560	15	17	12	18	62	62
	30	10	16	25	81	80
	50	12	18	31	85	86

a d'autre part une action catalytique évidente sur la fluoruration; cependant, la différence entre les résultats obtenus avec des mélanges contenant respectivement 10 et 20% d'hydrogène est insignifiante. On a ensuite effectué des essais complémentaires, non relatés ici, qui ont montré que cette teneur en hydrogène pouvait être ramenée à 5% environ sans modification sensible des résultats; par mesure de sécurité cependant, la suite des essais a été effectuée avec une teneur en hydrogène de 10% dans le mélange fluorant.

L'influence de la température et du débit de gaz est clairement décelable à la lecture du Tableau I, sans nécessiter d'autres commentaires. L'analyse chimique a montré que les résidus solides demeurant dans la nacelle après fluoruration sont formés essentiellement de TiO_2 ; d'autres analyses effectuées sur les condensats ont indiqué des teneurs en TiF_4 de 85 à 65% et des teneurs correspondantes en TiO_2 de 15 à 35%; la présence de TiO_2 dans la fraction volatile est imputable à une hydrolyse partielle du TiF_4 condensé, par suite de la présence de l'eau produite par la réaction. Les teneurs totales trouvées en oxygène et fluor ont été conventionnellement exprimées en % de TiO_2 et de TiF_4 , mais il est certain qu'une partie non négligeable de l'oxygène et du fluor se trouve sous la forme de l'oxyfluorure $TiOF_2$.

L'obtention de TiF_4 exempt d'oxygène n'est d'ailleurs pas un problème facile à résoudre; la teneur en oxydes du fluorure produit peut cependant être fortement réduite par l'application du mode opératoire décrit plus loin; on peut mentionner en outre qu'il existe un procédé possible, mais coûteux, consistant à dissoudre sélectivement TiF_4 dans la pyridine, tandis que TiO_2 et $TiOF_2$ restent insolubles, puis à éliminer le solvant par évaporation afin de le recycler.

Résultats des essais de fluoruration de Fe_2O_3

Dans ce cas, les essais ont été restreints aux conditions opératoires semblant les plus favorables pour la fluoruration de TiO_2 . Les résultats obtenus par pesée des résidus de la nacelle sont repris au Tableau II. On peut se rendre compte que les pertes en oxyde de fer ont été faibles.

TABLEAU II
PERTES EN FER (%) DU POIDS DE FER INITIALEMENT PRÉSENT)

Température (°C)	Débit de HF (g/h)	Composition du mélange gazeux (% vol.)	
		100% HF	90% HF + 10% H_2
480	30	4	3
	50	5	6
560	30	1.5	1.5
	50	1	1.5

Ce résultat favorable peut être imputé:

- (1) soit à une fluoruration nulle de l'oxyde de fer;
- (2) soit à la formation exclusive de fluorures de fer non volatils.

Comme tous les fluorures de fer connus n'ont pas de point d'ébullition sous la pression ordinaire, mais se décomposent par chauffage (alors que TiF_4 bout à 284°C), la seconde possibilité semblait la plus vraisemblable; pour vérifier cette hypothèse, on a effectué sur les résidus, des déterminations du fluor, dont les résultats, exprimés conventionnellement comme FeF_2 , sont reproduits au Tableau III.

TABLEAU III
TENEUR EN FeF_2 DES RÉSIDUS DE LA FLUORURATION DE L'OXYDE DE FER (% EN POIDS)

Température (°C)	Débit de HF (g/h)	Composition du mélange gazeux (% vol.)	
		100% HF	90% HF + 10% H_2
480	30	24	45
	50	31	48
560	30	18	25
	50	21	29

On peut conclure de ces résultats qu'une fluoruration partielle de l'oxyde de fer a lieu en réalité, mais que la majeure partie des fluorures reste dans la nacelle, ainsi que l'on pouvait s'y attendre.

La fixation d'un élément aussi coûteux que le fluor sur un métal aussi commun que le fer pouvait être un handicap sérieux pour ce procédé; mais l'élimination quasi complète du fluor fixé sur le résidu peut être réalisée en y faisant passer un courant d'hydrogène pur à une température appropriée; en alternative, au cas où il n'exis-

terait pas de débouché suffisant pour la poudre de fer réduit à l'hydrogène, on pourrait employer un courant de vapeur d'eau, de manière à transformer le résidu ferrique en un mélange d'oxydes de fer, utilisables comme minéral.

Résultats des essais de fluoruration de l'ilménite

Les essais, effectués seulement dans les conditions qui s'étaient avérées les plus intéressantes, ont donné les résultats indiqués (Tableau IV).

TABLEAU IV
PERTES DE POIDS DES ÉCHANTILLONS D'ILMÉNITE (% DU POIDS INITIAL)

Température (°C)	Débit de HF (g/h)	Composition du mélange gazeux (% vol.)	
		100% HF	90% HF + 10% H ₂
480	30	14	33
	50	16	35
560	30	13	37
	50	14	41

Pour l'examen des résultats du Tableau IV, il est nécessaire de tenir compte du fait que la perte de poids maxima possible est de 49%, ce qui correspond à l'élimination totale du TiO₂ présent initialement; en réalité, une perte de poids de 41% est relevée dans le cas le plus favorable.

D'autre part, du Tableau II il est permis de déduire que la perte de poids est imputable, à raison de 0.8% seulement au plus, à une volatilisation de l'oxyde de fer. Le rendement de la volatilisation du titane est donc dans ce cas de

$$\frac{40.2}{49} \times 100 = 83\%$$

On a déterminé en outre les teneurs en fluor des résidus de nacelle; les valeurs obtenues sont exprimées conventionnellement en FeF₂ au Tableau V.

Ces chiffres correspondent assez bien aux résultats du Tableau III; dans ce cas également, le fluor fixé en pure perte sur le fer peut être récupéré en faisant passer sur le résidu un courant d'hydrogène ou de vapeur d'eau.

TABLEAU V
TENEURS EN FeF₂ DES RÉSIDUS DE FLUORURATION DE L'ILMÉNITE (% EN POIDS)

Température (°C)	Débit de HF (g/h)	Composition du mélange gazeux (% vol.)	
		100% HF	90% HF + 10% H ₂
480	30	14	33
	50	12	35
560	30	11	21
	50	14	23

On a également déterminé la teneur en titane des résidus; les résultats obtenus peuvent se résumer en disant que 5% seulement du TiO_2 initial se retrouvent dans le résidu, en opérant dans les conditions les plus favorables.

Les condensats ont été aussi soumis à l'analyse; leur teneur moyenne en FeF_2 varie entre 3 à 7%, tandis que TiO_2 est compris entre 30 et 40%, le solde étant constitué de TiF_4 . Cette teneur élevée en oxyde peut être attribuée sans doute à une hydrolyse du fluorure par la vapeur d'eau produite pendant la fluoruration des oxydes de titane et de fer.

Résultats des essais de fluoruration de l'ilménite réduite

Les essais ont été restreints à l'emploi du mélange 90% HF + 10% H_2 et aux températures de 480 et 560°C, le débit de HF étant de l'ordre de 50 g/h.

Les pertes de poids constatées ont été respectivement de 33.4 et 42.5% du poids initial. Les teneurs en fluor des résidus, exprimées conventionnellement comme FeF_2 , sont 39 et 20.2%; la teneur en TiO_2 du résidu ne dépasse pas 3% du poids d'ilménite initial. D'autre part, les condensats présentent les compositions suivantes: en opérant à 480°C, FeF_2 , 1%; TiO_2 , 15%; TiF_4 , 84%; en opérant à 560°C, FeF_2 , 2%; TiO_2 , 9%; TiF_4 , 89%.

Par suite de la diminution de la quantité d'eau engendrée par la réaction, l'hydrolyse du condensat de TiF_4 est fortement réduite, comme le montrent les résultats ci-dessus.

En outre, l'utilisation d'ilménite préalablement réduite à l'avantage d'accroître la vitesse de fluoruration d'environ 30% par rapport aux essais avec l'ilménite brute.

Détermination de la température de fluoruration optima

Comme les températures de 400, 480 et 560°C, adoptées pour les essais, étaient trop espacées pour pouvoir fixer avec précision la température optima de fluoruration, on

TABLEAU VI
RÉSULTATS DE LA FLUORURATION DE L'ILMÉNITE NATURELLE ET RÉDUITE

Ilménite	Température de fluoruration (°C)	Perte de poids (% du poids initial)	Teneur en FeF_2 du résidu de la nacelle (% en poids)	Composition du condensat (% en poids)		
				FeF_2	TiO_2	TiF_4
Naturelle	500	39	78	4.2	41	54
	520	48	71	5.4	36	58
	540	43	62	4.6	33	62
Réduite	500	36	44	0.8	12	78
	520	51	41	1.2	10	88
	540	45	28	1.6	8	90

a effectué quelques essais supplémentaires aux températures de 500, 520 et 540°C; les résultats obtenus sont résumés au Tableau VI.

On peut conclure de ce tableau que la température optima pour la fluoruration de l'ilménite, brute ou réduite, se trouve aux environs de 520°C.

Conclusions des essais de fluoruration

Les essais effectués ont démontré que le fluorure d'hydrogène est un agent fluorant sélectif et efficace de l'ilménite, quand il est mélangé à 5% au moins d'hydrogène.

La température de réaction peut être choisie dans un domaine assez étendu, mais les meilleurs résultats correspondent à une température de 520°C environ.

Le titane est presque complètement volatilisé sous forme de tétrafluorure de titane et est condensé comme tel, avec cependant une rétrogradation partielle à l'état de TiO_2 ou de TiOF_2 causée par une hydrolyse. La fraction du HF fixée sur le résidu ferreux peut être récupérée par un balayage à l'hydrogène ou à la vapeur d'eau.

Quand on utilise de l'ilménite réduite à la place de l'ilménite brute, les résultats de la fluoruration connaissent une amélioration significative.

RÉDUCTION PAR L'HYDROGÈNE

Plan des recherches

Comme suite aux résultats intéressants fournis par les essais de fluoruration de l'ilménite préalablement réduite, on a voulu déterminer le mode opératoire le plus approprié pour effectuer cette réduction. Le seul réducteur envisagé a été l'hydrogène. Les facteurs étudiés ont été la température de réduction, le débit de gaz et la granulométrie des oxydes mis en oeuvre.

Ces essais avaient également pour but de déterminer si la réduction de l'oxyde de fer pouvait être complète et si cette réduction se produisait seule ou était accompagnée d'une réduction partielle du bioxyde de titane en oxydes inférieurs.

Ce problème a été étudié en recourant à la gravimétrie, à la diffraction aux rayons X et à l'analyse chimique.

Les essais de réduction préliminaires ont été effectués sur les oxydes simples; ils ont été complétés par des essais de réduction du minerai, constitué d'oxydes mixtes; ces derniers essais seront seuls rapportés ci-dessous.

Appareillage

L'appareil représenté à la Fig. 3 est prévu pour effectuer la réduction par étapes successives, de manière qu'après chaque étape, on puisse déterminer la perte de poids

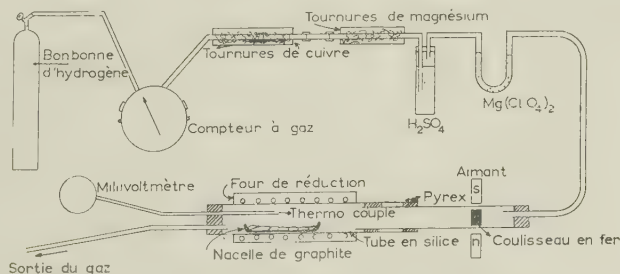


Fig. 3. L'appareil pour réduction par l'hydrogène.

et prélever éventuellement un échantillon pour l'analyse par diffraction aux rayons X.

Le four de réduction est constitué d'un tube en quartz de 20 mm de diamètre,

chauffé dans sa partie médiane par un enroulement en nichrome; la mesure de température est effectuée au moyen d'un thermo-couple en chromel-alumel utilisable dans le domaine de température étudié (500-1000°C).

L'hydrogène, fourni par une bonbonne, traverse un débitmètre, puis est débarrassé de son oxygène par un lit chauffé de copeaux de cuivre et de magnésium; il traverse ensuite un barboteur à acide sulfurique et une couche de perchlorate de magnésium qui éliminent son humidité.

Un courant d'azote sec peut être envoyé dans l'appareil à la place de l'hydrogène.

Mode opératoire

Un échantillon d'oxyde de 500 mg est étendu en couche mince uniforme dans une nacelle de graphite placée dans la zone froide du tube de quartz; la nacelle est alors reliée par un fil métallique à un coulisseau en fer doux, puis le four est fermé. On fait alors passer un courant d'azote dans le four pendant toute la durée de la mise à température; quand la température de l'essai est atteinte, un aimant permet de manoeuvrer le coulisseau de l'extérieur, de manière à introduire la nacelle dans la zone chaude; le courant d'hydrogène peut alors circuler pendant un temps déterminé, puis est à nouveau remplacé par de l'azote; la nacelle est alors retirée de la zone chaude de la même façon et est laissée à refroidir; elle est ensuite retirée du tube en vue de la pesée et de l'échantillonnage.

Matières premières

Les matières utilisées sont les mêmes que pour les essais de fluoruration.

Résultats des mesures gravimétriques

Quelques essais préliminaires ont montré que, dans les conditions opératoires utilisées, le débit d'hydrogène n'avait plus d'influence, ni sur le taux, ni sur la vitesse de réduction, au delà d'une limite située vers 3 l/min. C'est pourquoi, tout le travail expérimental subséquent a été effectué avec ce débit d'hydrogène, les températures choisies étant 500, 600, 700, 800, 900 et 1000°C.

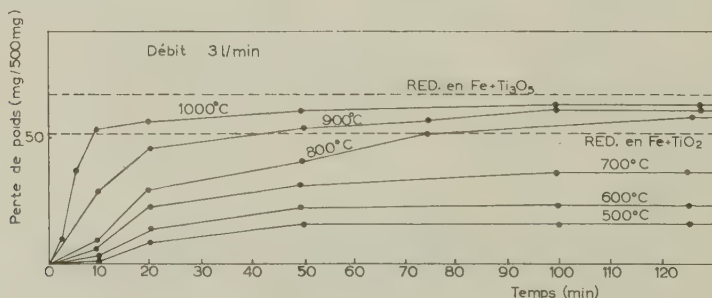


Fig. 4. Réduction de l'ilménite.

Pour le cas de la réduction de l'ilménite, les résultats des pesées des échantillons sont reproduits à la Fig. 4. Il convient de remarquer que les courbes de réduction (perte de poids en fonction du temps) présentent une allure en S caractéristique et

comportent trois sections, à savoir une période d'induction, une période de réduction rapide et une dernière période d'achèvement au ralenti de la réduction.

La granulométrie du minerai a peu d'influence sur la vitesse de réduction, sauf dans la dernière période, qui est raccourcie par l'emploi d'une poudre à granulation fine. L'accroissement de la température de réaction augmente à la fois la vitesse et le taux de réduction; on peut en conclure que la réduction complète de l'ilménite en $\text{Fe}+\text{TiO}_2$ exige pratiquement une température minima d'environ 750°C .

Des essais complémentaires effectués sur échantillons de 1000 g ont donné des résultats tout à fait concordants, notamment au point de vue de la température optima de réduction. La température adoptée de 750°C offre l'avantage supplémentaire d'une réduction insignifiante du TiO_2 en sous-oxydes, comme le montreront plus loin les résultats de l'analyse aux rayons X.

Résultats des analyses par diffraction aux rayons X

On a analysé différents échantillons par la méthode de DEBYE-SCHERRER. Les résultats reproduits au Tableau VII sont relatifs seulement aux échantillons pris à la fin de chaque essai de réduction.

Il est facile de se rendre compte que les constituants identifiés correspondent bien à ce qui pouvait être attendu d'après les mesures gravimétriques.

TABLEAU VII

RÉSULTATS DE L'ANALYSE AUX RAYONS X DES PRODUITS DE LA RÉDUCTION PAR L'HYDROGÈNE

Temp. de réduction ($^\circ\text{C}$)	Réduction de Fe_2O_3		Réduction de TiO_2		Réduction du FeTiO_3	
	Constituants principaux	Constituants accessoires	Constituants principaux	Constituants accessoires	Constituants principaux	Constituants accessoires
500	Fe_2O_3	Fe?	TiO_2 (rutile)	—	FeTiO_3	Fe, TiO_2 (rutile)
600	Fe_2O_3	FeO	TiO_2 (rutile)	—	FeTiO_3	Fe, TiO_2 (rutile)
700	Fe	FeO	TiO_2 (rutile)	—	FeTiO_3 , Fe TiO_2 (rutile)	—
800	Fe	—	TiO_2 (rutile)	—	FeTiO_3 , Fe TiO_2 (rutile)	FeTiO_3 , TiO_2 (anatase)
900	Fe	—	TiO_2 (rutile)	TiO_2 (anatase)	Fe, TiO_2 (rutile)	FeTiO_3 , TiO_2 (rutile)
1000	Fe	Fe_2O_3	TiO_2 (rutile)	Ti_3O_5	Fe, TiO_2 (rutile)	FeTO_3 , TiO_2 , Ti_3O_5

Conclusions des essais de réduction

Les essais décrits montrent la possibilité de transformer l'ilménite en un mélange de fer et de bioxyde de titane. En utilisant l'hydrogène comme réducteur et en choisissant judicieusement la température de réduction, il est possible d'éviter pratiquement toute réduction du TiO_2 en oxydes inférieurs.

REMERCIEMENTS

Qu'il nous soit permis d'exprimer ici notre gratitude à M. le Professeur DECROLY, de l'Université de Bruxelles, pour son appui et ses conseils dans l'exécution de ce travail.

Il convient aussi de mentionner que l'enrichissement magnétique préalable a été effectué dans le laboratoire de M. le Professeur DE MAGNEE, de la même Université.

M. COUVREUR, de la Société Cofinindus, a eu l'obligeance de mettre à notre disposition la titanomagnétite utilisée comme matière première.

BIBLIOGRAPHIE

Bien que de nombreux articles, brevets et traités aient été publiés dans le domaine du traitement des minerais titanifères, les références particulières relatives à la fluoruration de ces minerais sont pratiquement inexistantes.

Toutefois, le présent travail a été effectué en se basant sur des travaux préliminaires non publiés exécutés à l'Université Libre de Bruxelles.

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HOT WORKING OF NIOBIUM ALLOYS

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SUMMARY

The hot working characteristics of several two-phase niobium-carbon alloys have been investigated and the results are discussed in terms of solid solution hardening and dispersion hardening.

INTRODUCTION

Many elements added to niobium to improve its resistance to oxidation or its mechanical properties harden the material to such an extent that cold working is difficult or impossible. Often the ductility of these alloys would be improved if precipitates could be broken down and redistributed and if the overall grain size could be refined. Hot deformation is the most obvious method of achieving this objective and many attempts are being made to develop methods of extruding and forging these alloys.

This investigation was designed to give information on the types of problem which are likely to be encountered in working two-phase alloys. Niobium-carbon alloys were chosen as they could easily be prepared in an argon arc furnace.

EXPERIMENTAL

The most convenient means of investigating, on a laboratory scale, the forging characteristics of niobium alloys appears to be by the use of a small upset forging press. In the design of this apparatus it was necessary to consider the following factors.

(1) Rapid oxidation and contamination of niobium above 300°C make an inert atmosphere absolutely essential for forging at high temperatures.

(2) Rapid cooling of small ingots implies that a rapid transfer from the heater to the press is necessary.

(3) Specimen temperature must be easily measured.

(4) Anvils must be able to withstand surface temperatures of the order of 1700°C and retain some strength.

These requirements led to the decision to enclose the press and ingot heating arrangements in a chamber which could be evacuated and filled with an inert atmosphere (Fig. 1). The press was built round a 4-ton screw jack which was chosen for its ease of manipulation by one revolving shaft. A frame was constructed from two 1-in. thick discs of mild steel, 12 in. in diameter separated by four 1-in. diameter steel rods. These rods were screwed into the lower plate and passed through the top plate

which was retained in position by means of nuts screwed onto the rods. The jack was centred on the lower plate and the top anvil was screwed into the upper plate. Anvils machined from massive molybdenum were set with their working surfaces parallel. The jack was operated by a revolving shaft incorporating a universal joint; a double O-ring seal was used to take the shaft through the wall of the chamber. The load applied to the jack shaft was fixed by means of a preset torque wrench and the temperature of the specimen was obtained by means of an optical pyrometer sighted through a viewing port one at side of the chamber.

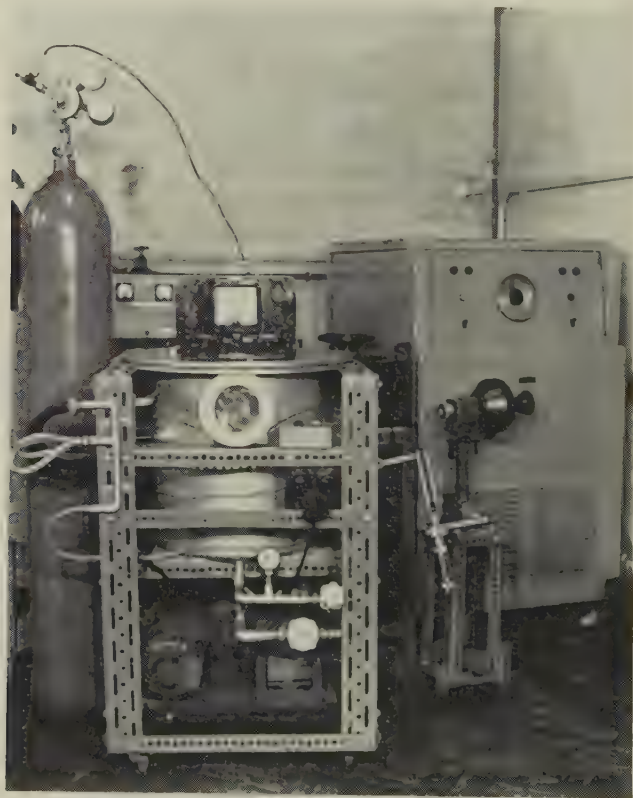


Fig. 1. General view of the forging unit.

A simple 5-turn radio-frequency induction coil was used to heat the specimen and a clear silica tube was placed between the coil and the specimen to prevent arcing. Specimens were held in a $\frac{3}{8}$ in. diam. molybdenum holder and could be fixed in position by a spring clip or pin (Fig. 2).

A calibration of the pyrometer was carried out by placing a thermocouple in a dummy specimen. In the temperature range 1200–1600 °C the pyrometer correction was approximately +25 °C. However, during the 0.5 sec required to transfer the specimen from the coil to the press the temperature was observed to fall by approxi-

mately 25°C and the pyrometer readings thus gave the approximate temperature at the start of forging. The load on the anvils was determined by comparing the deformations produced in small aluminium specimens by compression in a conventional testing machine with that obtained in the press. A standard torque of 20 ft. lb. was used for the experiments on niobium-carbon alloys and this corresponded to a load of 1.85 tons on the anvils.

The leak rate of the degassed chamber was 0.006 lusec* and the ultimate vacuum obtained with a rotary pump was 8 μ Hg. Before use, the chamber was purged in the

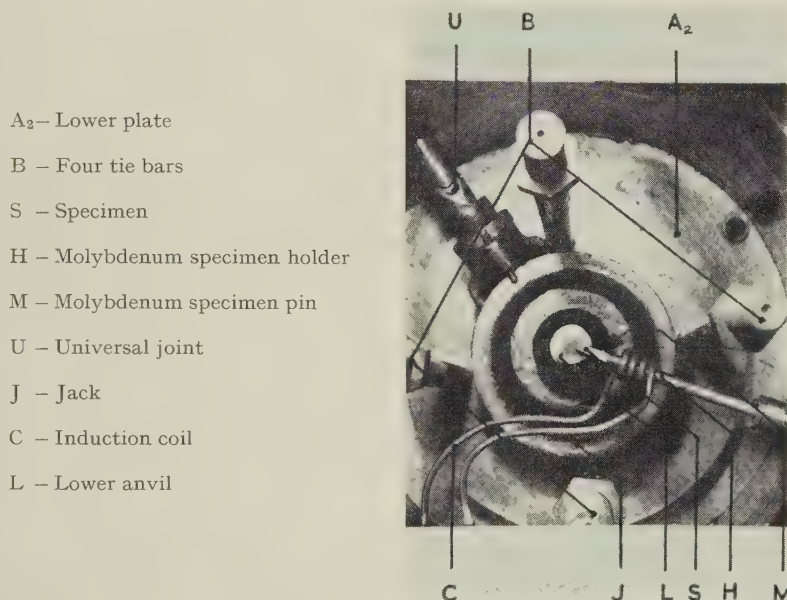


Fig. 2. View inside the inert atmosphere forging unit. (The top plate A_1 , the upper anvil, and the silica tube (see Fig. 9) have been removed.)

following manner; the chamber evacuated to 100 μ Hg filled with $\frac{1}{3}$ atmosphere argon and re-evacuated to below 25 μ Hg three times, with intermediate flushes of argon to 500 μ Hg. The apparatus was then filled to $\frac{1}{3}$ atmosphere of argon before use. Throughout the work the argon used was supplied by B.O.G. and was stated to be of 99.995% purity.

The alloys were made from: Commercial niobium (C, 0.01–0.02%; Ta, 0.5–1.2%; Fe < 0.07%; and O_2 , 0.02–0.03%) and sintered niobium rondelles (C, 0.2%; Si, 0.025%; Fe, 0.025%; W, 0.03%) supplied by Murex Ltd. and reactor grade A graphite.

A non-consumable tungsten electrode argon arc furnace was used to produce ingots 0.3-in. diam. and about 1.2 in. long. These were machined to give blocks 0.2 $\times$ 0.2 $\times$ 1 in. and a hole was drilled at one end to enable the block to be pinned into the holder.

* To obtain this low leak rate all internal metal surfaces except the molybdenum anvils and the water-cooled stainless steel porter bar were coated with a Bakelite resin.

To assess the forgeability of an alloy a stop on the porter bar was adjusted to allow only $\frac{1}{4}$ in. of the specimen to enter the anvils. After purging the chamber, each specimen was annealed for approximately three minutes before forging. As soon as the power was switched off the porter bar was pushed to the limit stop and the jack handle was turned at an approximately constant rate. When the torque reached the required value the wrench was immediately turned back and the pressure on the specimen released. The forged specimen was removed when cold, measured and a correction was applied to allow for small variations in the area over which the load was applied. This correction was deduced from Tresca's Law and all the reductions were related to 0.05 sq.in.

Microspecimens were prepared by wet grinding on successive grades of silicon carbide paper to 600 A and then using a polish attack solution of 2 g of gamma alumina in 90 ml of saturated ferric chloride and 10 ml of hydrofluoric acid.

RESULTS AND DISCUSSION

Alloys containing 0.1% C, 0.2% C and 0.5% C all give virtually the same plot of percentage reduction against temperature (Fig. 3). These curves all show a dip at about 1500°C and the 1% C alloy joins the general trend for temperatures greater

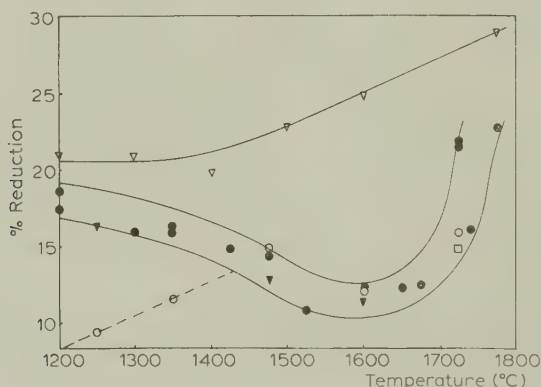


Fig. 3. Graph showing all the forging test results. ▽, 0.01% C; ▼, 0.1% C; ●, 0.2% C; □, 0.5% C; ○, 1.0% C.

than 1350°C. Commercial niobium containing about 0.01% C shows greater reductions than the carbon-containing alloys and a comparatively rapid increase in the amount of deformation at temperatures above 1300°C. The carbon-containing alloys show a similar increase at about 1550°C.

The carbon contained in the commercial niobium is all present in solid solution, whereas the other alloys probably contain excess carbides at all of the forging temperatures. The microstructures of the cast alloys containing 0.1–0.5% C are similar (see Figs. 4–6), whereas the microstructure of the alloy containing 1% C is markedly different (Fig. 7). The general shape of the curves shown in Fig. 4 suggests that three processes may be involved. At temperatures up to 1350°C the morphology of the precipitate appears to influence the deformation and this may possibly indicate

that deformation is climb-controlled and that the interparticle spacing is important. At higher temperatures, where diffusion is rapid, climb is no longer a rate-controlling process and the morphology of the precipitate becomes unimportant and the rate



Fig. 4. Niobium-0.1% carbon alloy, as-cast.
($\times 300$)



Fig. 5. Niobium-0.2% carbon alloy, as-cast.
($\times 300$)

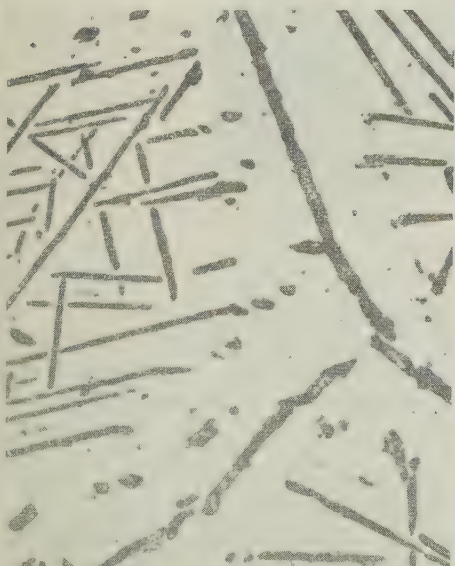


Fig. 6. Niobium-0.5% carbon alloy, as-cast.
($\times 300$)

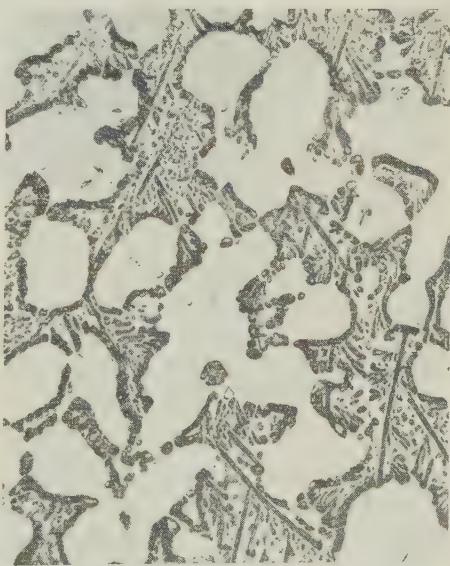


Fig. 7. Niobium-1.0% carbon alloy, as-cast.
($\times 300$)

of deformation is then mainly controlled by the strength of the matrix. The gradual decrease in the % reduction up to 1500°C would then be associated with the increasing amounts of carbon present in solid solution. At temperatures greater than



Fig. 8. Niobium-0.2% carbon alloy, forged by one press at 1675°C. ($\times 200$)

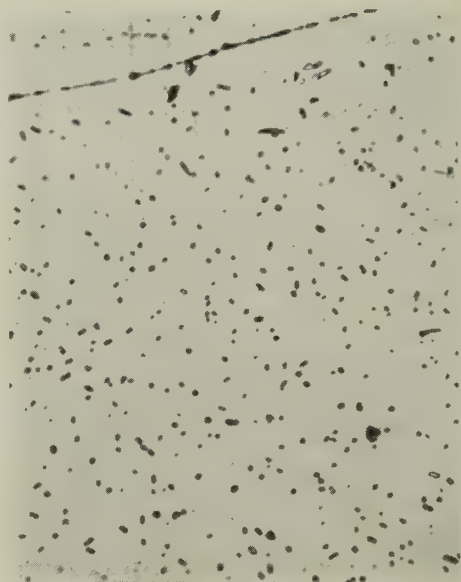


Fig. 9. Niobium-0.2% carbon alloy, forged by one press at 1640°C. ($\times 200$)

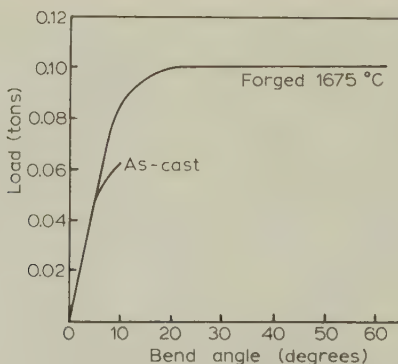


Fig. 10. Stress-strain curves obtained in a slow bend test on a Hounsfield testing machine, for cast and forged specimens of an alloy of niobium with 0.2% carbon.

1650°C in the case of alloys containing 0.1 to 1% C and 1300°C in the case of commercial niobium recrystallisation is probably taking place at the same time as deformation. Figures 8 and 9 show carbide precipitates on grain boundaries or sub-grain boundaries in a 0.2% C alloy forged at 1675°C but not in one forged at 1640°C.

These carbide precipitates are probably induced after forging. The forging load

on the specimen was, in each case, released immediately the preset value had been attained and thus the cooling of the specimens by the anvils diminished. Considerable heat was stored in the part of the specimen not gripped by the anvils and this was sufficient to reheat visibly the forged end and allow precipitation.

An interesting sidelight of the present investigation was that the alloys forged at temperatures greater than 1500°C all apparently contained less carbide than the as-cast alloys and therefore were cooled more rapidly from the forging temperature than the castings. Examination of 0.2% C specimens rapidly water-quenched from 1250°C and 1475°C confirmed this view.



Fig. 11. Niobium-0.2% carbon alloy. Bend test fractures: (a) as-cast; (b) forged 1675°C .

The difference in cooling rates of the castings and forgings makes comparison of mechanical test results difficult, but generally the forged material required higher stresses to produce a given deformation (Fig. 10). This is in agreement with suggestion that the forged alloys contain a higher percentage of carbon in super-saturated solution than the castings. The fracture surfaces of the alloys showed clearly the refinement in grain size associated with forging at 1675°C (Fig. 11).

ACKNOWLEDGEMENTS

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PHASE EQUILIBRIA IN THE THORIUM-TANTALUM SYSTEM*

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SUMMARY

X-ray, electrical resistance, thermal and metallographic methods were used to determine the phase diagram of the thorium-tantalum system. The diagram is of the simple eutectic type with a eutectoid reaction associated with the thorium α - β transformation. The eutectic point occurs at $1565 \pm 10^\circ\text{C}$ and 4.0 ± 0.5 wt.% tantalum. No evidence of intermetallic compounds was found and only slight terminal solid solubility was found at either end of the diagram, even at elevated temperatures. The solubility of tantalum in thorium at the eutectic temperature is about 0.4 wt.% and below 1340°C is less than 0.2 wt.%. The solubility of thorium in tantalum was found to be less than 0.2 wt.% at the eutectic temperature.

INTRODUCTION

This investigation was undertaken in order to establish the constitutional diagram of the thorium-tantalum alloys and to increase the knowledge of thorium and tantalum metallurgy, CHIOTTI¹ has reported that thorium has a face-centered-cubic structure at temperatures up to $1360 \pm 10^\circ\text{C}$ and a body-centered-cubic structure from 1360°C to the $1750 \pm 10^\circ\text{C}$ melting point. The lattice spacing for the face-centered-cubic form at room temperature is $5.0843 \text{ \AA}$ according to EVANS AND RAYNOR². WILLIAMS AND PECHIN³ report that tantalum exists in the body-centered-cubic form up to the 2940°C melting point.

The behavior of tantalum upon alloying with thorium and other elements is predicted by MILLER⁴. The collective results from several considerations predicted that thorium is a marginal case for liquid immiscibility with tantalum. Also, the size factor of thorium is unfavorable for solid solution formation and compounds are unlikely to form with tantalum. That the thorium-tantalum alloy system is most probably of the eutectic type was deduced from the diagrams of the thorium-group V-B alloy systems as compiled by ROUGH AND BAUER⁵.

PREPARATION OF ALLOYS

Component metals

The tantalum used in the preparation of the alloys was supplied by the Fansteel Metallurgical Corporation and was specified as high purity sheet. The impurity content of this metal and that of the thorium is given in Table I. The crystal-bar

* Contribution No. 1016. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

thorium used in this investigation was prepared by McMASTERS in the Ames Laboratory. The iodide process as described by VEIGEL *et al.*⁶ was duplicated on a 200–300 g batch basis.

TABLE I
ANALYSIS OF THE COMPONENT METALS

Impurity element	Content in tantalum (p.p.m.)	Content in thorium (p.p.m.)
Carbon	16*	75–100*
Oxygen	50**	50–150**
Nitrogen	22**	75–150*
Hydrogen	1**	4**
Iron	40*	<20

* Chemical analysis.

** Vacuum fusion analysis.

Spectrographic analysis for: (1) tantalum, Ti and Si <20 p.p.m., Mg and Nb—faint trace; (2) thorium, Mn, Al, Be, Ca, Mg, Si, Zr, and Ni—below lower limit of standards, usually <20 p.p.m.

Melting and homogenizing

A tungsten-electrode arc-furnace, as described by LEVINGSTON AND WILLIAMS⁷, was used to melt the alloys. Charges of intended compositions were melted several times and were turned over between melts in an attempt to make them homogeneous. Weight losses during the melting procedures were negligible and the data from this investigation are based on the intended compositions. The large difference between the melting points of the component metals made melting and homogenizing of the alloys difficult. Splattering of the molten charge necessitated power reductions in the arc in order to avoid sample losses and to facilitate ingot shaping. The resulting ingots were not homogeneous since the lower melting eutectic constituent tended to form a shell around the higher melting center portion which was dendritic in nature. Cold working and homogenizing heat treatments usually preceded the taking of data.

Fabrication

Melting point bars, as shown by WILLIAMS⁸, were prepared by milling. Resistance-temperature specimens were prepared by swaging 0.250-in. diameter arc-cast rods into 0.030-in. wires. Flaking of the dendritic phase during swaging of 10-mil wire to be used for X-ray diffraction specimens was avoided by choosing samples in the 1.0–10 and 90–99 wt.% Ta–Th composition ranges.

APPARATUS AND PROCEDURES

Melting point determinations

The apparatus and procedure used to obtain solidus data have been described by WILLIAMS⁸. The eutectic temperature data obtained from the necked-down bar specimens were determined by observing the temperature at which the molten metal disrupted the black-body conditions by causing a dark spot to appear at the bottom of the pyrometer sight hole. The liquidus lines were located by observing the temperature at which the specimens melted in two. Since only surface temperatures are

available above the solidus, the liquidus temperatures were corrected for emissivity by extrapolating the black-body *versus* surface temperature data obtained below the solidus. The extrapolation required the assumption that the surface temperature dependence of the emissivity is the same both below and above the solidus temperature.

Electrical resistance versus temperature

The apparatus, basic circuit and procedure used to obtain resistance-temperature data are reported by ROGERS AND ATKINS⁹. Two specimens, usually one thorium and the other a thorium-tantalum alloy, were connected in series with a standard resistor and a 6-volt storage battery. Ten-mil diameter tantalum potential leads were spot welded, under a helium atmosphere, to the specimens. The specimens were heated under vacuum in an electric furnace having silicon-carbide resistance heating elements. Resistance values were determined by measuring the voltage drop across the specimens and the standard resistance. The temperature was measured by a Pt-Pt + 13% Rh thermocouple giving data over a range from 30°C to 1425°C.

X-ray diffraction methods

Powders were filed from the melting point specimens and given a stress-relief anneal at 650°C for 36 hours. Thin sheet specimens prepared by rolling were stress-relieved by heat treatments prior to quenching and were used in conjunction with a focusing back-reflection camera. A diffractometer was used for phase identification in some metallographic specimens using standard procedures.

The more significant X-ray data were obtained from quenched wire specimens using a Debye-Scherrer camera and copper $K\alpha$ radiation. Ten-mil diameter wire specimens were heated by their own resistance between two water-cooled copper electrodes and quenched by thermal conduction when the power was turned off.

Metallography

The polishing and etching procedures were complicated by the nature of the alloys. The eutectic constituent is more readily attacked by etchants than is either dendritic phase, thus leaving the dendrites in relief. An electropolish was used in the final stages in order to avoid the scratches produced by the mechanical polishing.

A cathodic etching apparatus described by CARLSON *et al.*¹⁰ was used for some of the metallographic specimens.

EXPERIMENTAL RESULTS

Solidus and liquidus data

Melting point determinations were used to establish the temperature of the eutectic reaction isotherm and to approximate the position of the liquidus lines. The data listed in Table II and plotted in Fig. 1 placed the eutectic temperature at $1565 \pm 10^\circ\text{C}$. The liquidus data are listed in Table II and the liquidus lines appear as dashed lines in the diagram, since the data were only reliable to about $\pm 50^\circ\text{C}$.

Effects of tantalum on the transformation of thorium

Resistance-temperature data and X-ray diffraction results were used to determine the nature of the reaction associated with the allotropic transformation of thorium. This portion of the diagram is shown in the insert in Fig. 1.

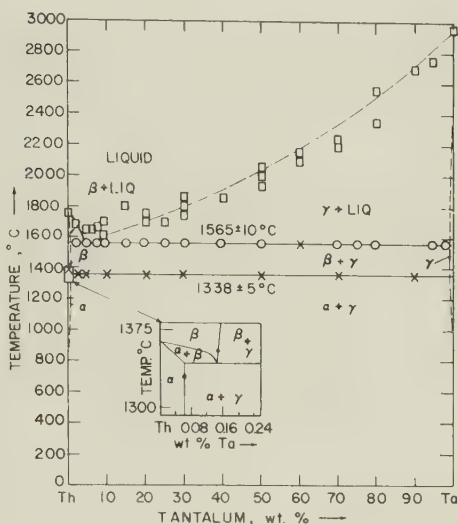


Fig. 1. Plot of data from which the thorium-tantalum diagram was drawn. $\circ$, solidus data from melting point determinations; $\square$, liquidus data from melting point determinations; $\times$, electrical resistance *versus* temperature results; $\bullet$, data from X-ray diffraction patterns.

TABLE II
DATA FROM THE MELTING POINT DETERMINATIONS

Wt. % Ta-Th	Solidus($^{\circ}$ C)	Liquidus($^{\circ}$ C)
thorium	melting points of 1700° C and 1725° C	
3.1	1563*	1685
5.0	1565*	1640
6.0	1565	1650
7.5	1563*	1620
9.0	1563	1680
10.6	—	1700
15.0	1565	1800
20.0	1565*	1725
25.0	1570**	1700
30.0	1566**	1800
40.0	1565	1850
50.0	1566**	1975
60.0	—	2125
70.0	1573	2230
75.0	1568	2025
80.0	1568*	2475
90.0	1570	—
95.0	1570	2750
98.0	1575	—
tantalum	melting point 2940° C†	

* Average of two measurements.

** Average of three measurements.

† Reported by WILLIAMS AND PECHIN³.

Table III lists the results obtained from several resistance-temperature experiments and Fig. 2 is a plot of the data from a typical experiment. The temperature of the transformation in pure thorium was obtained by averaging the heating curve

TABLE III
RESISTANCE-TEMPERATURE DATA

Experiment number	Composition	Transformation heating (°C)	Temperature cooling (°C)
1	Th	1365	—
	10.0 wt. % Ta	1335	—
2	Th	1367	1362
	10.0 wt. % Ta	1338	—
3	Th	1369	1373
	20.0 wt. % Ta	1339	1342
4	Th	1360	1358
	10.0 wt. % Ta	1338	1342
5	Th	1365	—
6	Th	1368	1353
	3.2 wt. % Ta	1339	1335
7	7.5 wt. % Ta	1338	1333
average for unalloyed thorium		1363 $\pm$ 10°C	
average for alloyed thorium		1338 $\pm$ 5°C	

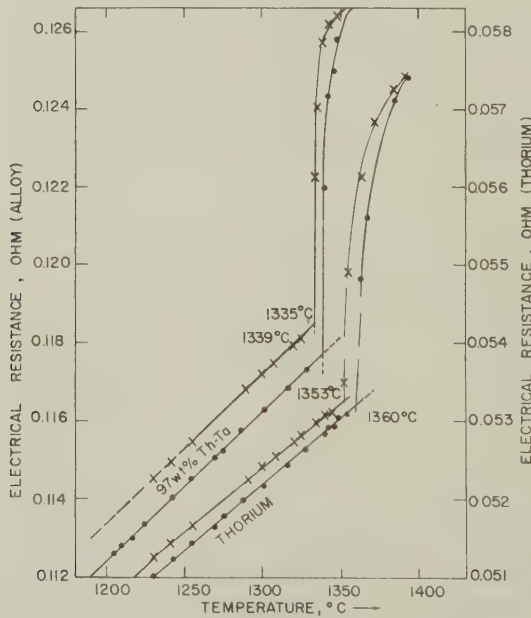


Fig. 2. Electrical resistance *versus* temperature graphs for unalloyed thorium and 3 wt.% Ta-Th specimens. ●, heating data; ×, cooling data.

and cooling curve values from several runs and is 1363 $\pm$ 10°C. A temperature of 1338 $\pm$ 5°C was obtained in a similar manner for the alloyed specimens. The addition of tantalum to thorium thus lowers the transformation temperature and a eutectoidal

arrangement is strongly suggested. The greater precision of the data for alloy samples suggests that some of the tantalum may be removing carbon from solution in the thorium to give Ta_2C ¹. While the presence of carbon or other impurities may thus be affecting the transformation temperatures observed, it is not expected that the form of the diagram is other than eutectoidal.

X-ray diffraction data obtained from quenched wire specimens yielded solubility values that are in agreement with the suggested eutectoidal arrangement. Precautions were taken to minimize the contamination of the freshly prepared specimens used in the final analysis. Three X-ray patterns from different portions of each quenched wire were measured and the lattice parameters calculated from the individual reflections (a_{hkl}) were averaged. These average a_{hkl} values and their corresponding Nelson-Riley functions were used to calculate a_0 by the method of least squares, as described by CULLITY¹¹. These lattice parameters are listed in Table IV. The

TABLE IV
SOLUBILITY DATA OBTAINED BY X-RAY DIFFRACTION METHODS

Composition	Temperature before quench ± 15°C	a_0 (Å)	Δa_0 (Å)	Solubility (wt.%)
Thorium	1330	5.0853		
	1375	5.0855		
5.1 wt. % Ta	1330	5.0846		
	1375	5.0838		
10.0 wt. % Ta	1330	5.0848		
	1375	5.0844		
				Ta in Th
Alloyed thorium (average)	1330	5.0847	0.0006	0.06
	1375	5.0841	0.0014	0.15
Tantalum	1350	3.3030		
				Th in Ta
95.0 wt. % Ta	1350	3.3032	0.0002	0.02

solubility data given in Table IV resulted from the calculations based on the lattice parameter values assuming that Vegard's Law holds for this dilute solution case. Calculations included correction factors for co-ordination numbers and for atomic diameter differences. Solubilities of Ta in Th are based on the computation which shows that 1.0 wt. % Ta dissolved in Th produces a lattice contraction, Δa_0 , of 0.0092 Å. A lattice parameter of 5.0854 ± 0.0004 Å was determined for unalloyed thorium by averaging values obtained from several specimens quenched from various temperatures. EVANS AND RAYNOR² listed a number of lattice parameters reported by various investigators and discussed the necessary precautions that must be taken if accurate values are to be obtained. The evidence of their work pointed toward an a_0 of 5.0843 Å as the preferred lattice spacing for iodide thorium at room temperature.

The solubility and resistance-temperature data are consistent with the requirements of a simple eutectoidal arrangement but the effort required to obtain the additional information needed to positively establish such an arrangement did not appear to be warranted in light of its limited contribution to the practical value of the investigation. Thus a simple eutectoidal arrangement was postulated as the most probable form of this reaction as shown in Fig. 1.

Solubility limits

On the basis of the data of Table IV, the β to $\beta + \gamma$ solvus in the eutectoidal region of the diagram has been placed at less than 0.2 wt. % Ta–Th. A solubility of 0.4 wt. % Ta–Th at the eutectic temperature was estimated from diffraction data



Fig. 3. 6 wt. % Ta–Th. γ -Tantalum solid solution dendrites in a eutectic matrix.

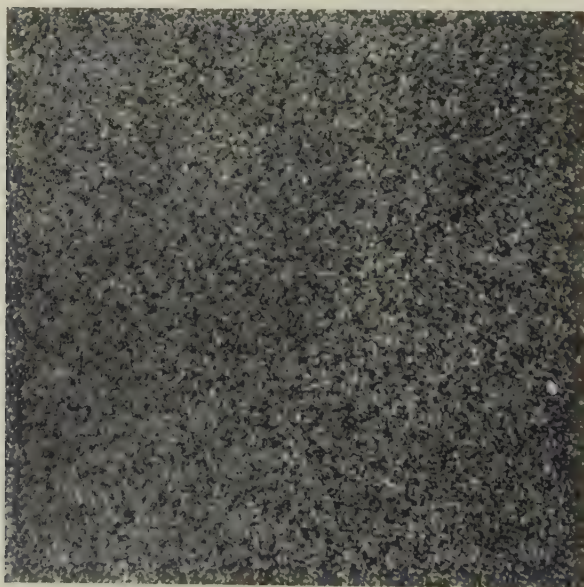


Fig. 4. 4 wt. % Ta–Th. Eutectic.

Above samples etched by swabbing the surfaces for one minute with a 1:5 conc. nitric acid–water solution to which was added 0.25 g sodium fluosilicate for each 100 ml.

of α -thorium obtained from samples quenched from 1525°C. As indicated by the parameter values, there is virtually no solid solubility of thorium in tantalum at 1350°C. Less than 0.2 wt.% Th in Ta at the eutectic temperature was detected by use of back-reflection equipment.

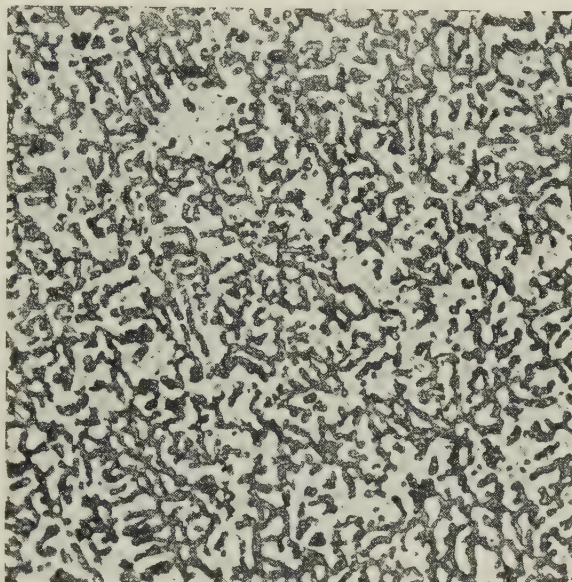


Fig. 5. 2 wt.% Ta-Th. α -Thorium solid solution (light) in a eutectic matrix. ($\times 500$)

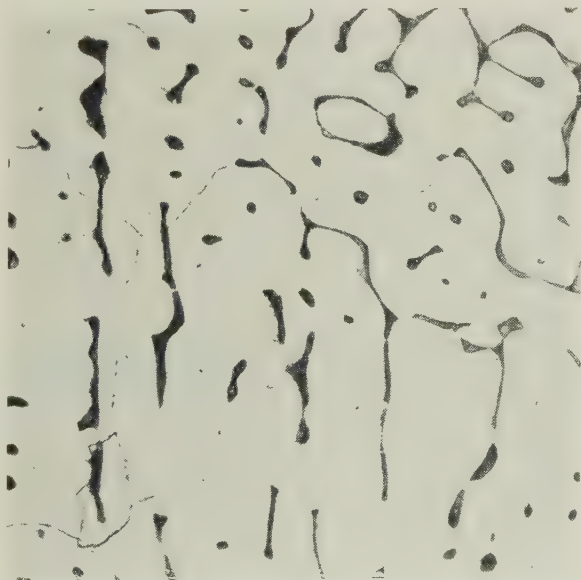


Fig. 6. 1 wt.% Ta-Th. α -Thorium solid solution plus eutectic (dark). ($\times 500$)

Above samples etched electrolytically. Electrolyte: 1:1 85% orthophosphoric acid-90% formic acid. Exposures of 30 sec. at 35 V and 0.6 A. All samples are in their as-cast condition.

Room temperature solubility data were obtained by X-ray diffraction methods using powder specimens. No differences in parameter values could be detected between alloyed and unalloyed specimens, so it was concluded that the solubility at room temperature must be less than 0.1 wt. % on both sides of the diagram.

Metallographic results

Metallography was used to establish the eutectic composition. The as-cast structures of samples with decreasing amounts of tantalum were observed microscopically. The eutectic composition was approached from the tantalum-rich side since the gamma tantalum dendrites that formed on freezing were easily identified. The eutectic composition pictured in Fig. 4 was established at 4.0 ± 0.5 wt. % Ta-Th by this method. The 6 wt. % Ta-Th microstructure shown in Fig. 3 exhibits a few γ -Ta dendrites and the 2 wt. % Ta-Th microstructure shown in Fig. 5 displays thorium solid solution in a eutectic matrix. A relatively harsh electrolytic etching treatment was required to disclose the thorium solid solution, while the γ -Ta dendrites were prominent after the application of a mild etchant for a brief period of time.

All alloy samples prepared in this investigation exhibited two-phase microstructures. The microstructure of an arc-cast 1 wt. % Ta-Th sample is shown in Fig. 6. Samples of compositions 1 wt. % Ta-Th and 99 wt. % Ta-Th which were heat-treated at 1300°C and 1540°C for several hours displayed two-phase microstructures which were not detectably different from those of the arc-cast samples. Therefore, solubility limits of less than 1 wt. % at 1540°C were deduced from this analysis.

ACKNOWLEDGEMENTS

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REACTIONS OF ORTHO-ESTERS OF TITANIUM

IV. SALICYLALDEHYDE DERIVATIVES OF TITANIUM

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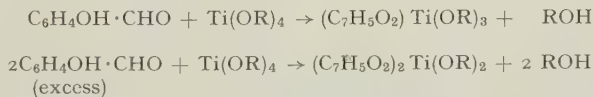
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SUMMARY

The reaction of salicylaldehyde with ethyl, isopropyl and *tert.*-butyl ortho-titanates and titanium tetrachloride has been found to yield disalicylaldehyde derivatives by straightforward exothermic reactions. The ethyl and isopropyl products have been shown to undergo an intramolecular Meerwein-Ponndorf type of oxidation reaction.

INTRODUCTION

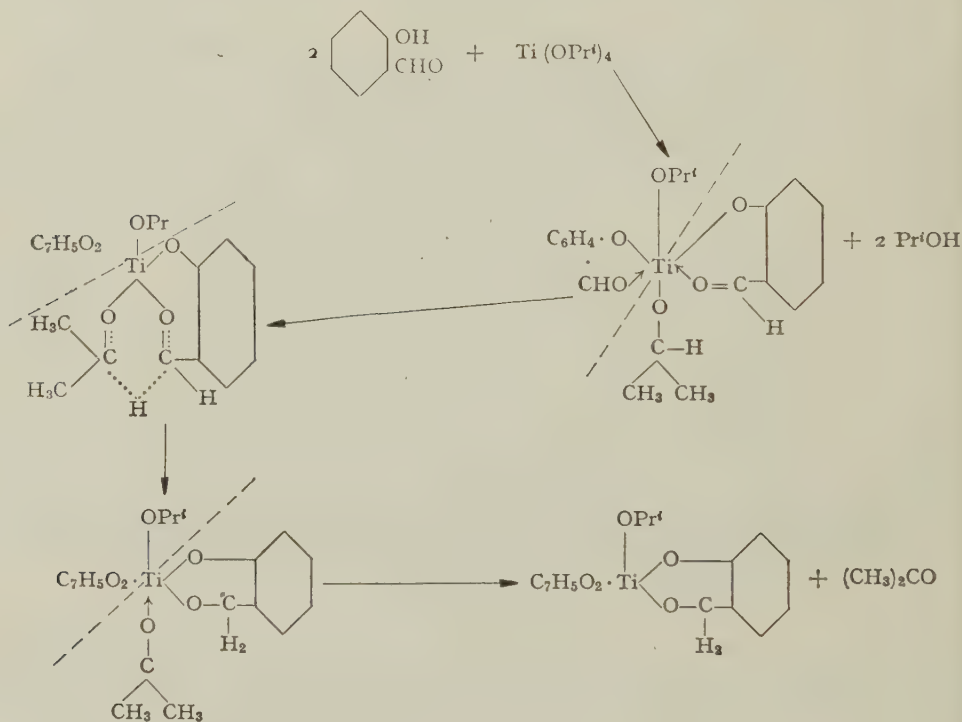
In view of the interesting properties shown by ethyl acetoacetate and acetyl acetone derivatives of titanium¹, the reactions between salicylaldehyde and alkyl ortho-titanates (ethyl, isopropyl and *tert.*-butyl) and titanium tetrachloride have been studied and the following exothermic reactions have been shown to occur quantitatively at room temperature:



(R = Et, Prⁱ and Bu^t)

The new compounds: (a) (C₇H₅O₂) Ti(OPrⁱ)₃, (b) (C₇H₅O₂) Ti(OEt)₂, (c) (C₇H₅O₂)₂ Ti(OPrⁱ)₂ and (d) (C₇H₅O₂)₂ Ti(Obu^t)₂ are yellow solids or thick liquids, soluble in benzene. Whereas (d) is stable when stored or when heated in boiling benzene, (a), (b) and (c) turn orange in diffused light and evolve acetaldehyde or acetone. The decomposition of (c) was followed by carrying out the reaction between Ti(OPrⁱ)₄ and C₆H₄OH·CHO (molar ratio 1 : 2) in boiling toluene and fractionating out the liberated isopropanol and acetone. These were estimated in the form of their 2,4-dinitrophenylhydrazine derivatives, the former after oxidation by dichromate². As was suggested by JACKMAN AND MACBETH³, for the reduction with aluminium isopropoxide the liberation of acetone in the reaction can be understood on the basis of hydrogen

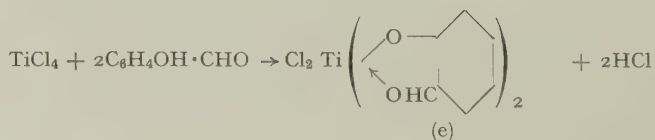
transfer through the formation of a cyclic six-membered ring, represented schematically for a half molecule as follows:



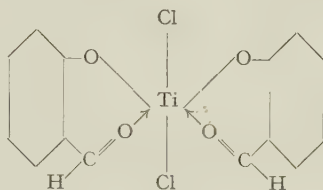
It is evident from the above representation that the *tert.*-butyl group (devoid of any hydrogen attached to its central carbon atom) is incapable of effecting the above type of reaction.

The thermal decomposition of (d) under reduced pressure was also studied with a view to obtaining the tetrasalicylaldehyde derivative of titanium. The compound was found to disproportionate giving $\text{Ti}(\text{O}i\text{Bu})_4$ (b.p. $92-93^\circ/4$ mm) and a non-volatile residue, which decomposed on further heating, even under reduced pressure. The tetrasalicylaldehyde derivative, however, could not be obtained at any stage.

The reaction of excess salicylaldehyde (>4 moles) with titanium tetrachloride in refluxing benzene was next attempted with a view to preparing the tetrasalicylaldehyde derivative. It was found to yield finally a chocolate-brown microcrystalline powder



The compound (e) was further refluxed with a fresh quantity of salicylaldehyde, but the unchanged nature of the product showed that no further replacement of chlorine takes place. The inability of compound (e) to react further with salicylaldehyde is in sharp contrast with the reaction of titanium tetrachloride with phenols⁴ to give tetraphenoxy derivatives and is similar to the reaction of titanium tetrachloride with acetylacetone⁵. By analogy with the structure proposed for the acetylacetone derivative the dichloride disalicylaldehyde derivative may also be assigned the plausible structure:



It has been possible to confirm the above findings by preliminary measurements of molecular weights ebullioscopically in benzene or toluene, although the very solubility of the derivative in most organic solvents limits the accuracy of these determinations. Further, the di-*tert*-butoxy disalicylaldehyde derivative has been shown to be monomeric in boiling benzene.

EXPERIMENTAL

Apparatus

Glass apparatus with interchangeable standard ground glass joints was employed throughout. Moisture was carefully excluded in all experiments. Molecular weight measurement was carried in a Gallenkamp semi-micro ebulliometer using a thermistor.

Materials

Benzene, toluene, ethyl and isopropyl orthotitanates were purified as described⁶. Preparation of *tert*-butyl orthotitanate was achieved by alcoholysis of ethyl orthotitanate, b.p. 64.5°/0.4 mm; found, Ti 14.0%; calc. for Ti (OBu^t)₄, Ti, 14.1%. Salicylaldehyde (B.D.H., Lab. reagent) was purified by distillation, b.p. 196.5°.

Reaction between isopropyl orthotitanate and salicylaldehyde; molar ratio 1:1

2.93 g (24.02 mmoles) salicylaldehyde was added to a well-cooled solution of isopropyl orthotitanate (6.92 g, 24.34 mmoles) in benzene (5.0 g). An exothermic reaction occurs. The light yellow solution was allowed to stand at room temperature under reduced pressure (1–1.5 mm) for 3 h. A thick, viscous, light yellow liquid (8.3 g), soluble in benzene, was obtained. Found: Ti, 13.9%. (C₆H₄O·CHO)Ti(OPrⁱ)₃ requires Ti, 13.8%. After a fortnight this compound develops a characteristic smell and becomes an orange-red semi-solid. 7.5 g of this substance was refluxed with 30.0 ml benzene for 11 hours. After drying the product at 65° at a pressure of 1.0 mm a very thick, viscous, red liquid (7.2 g) was obtained. Found: Ti, 14.9%.

Reaction between isopropyl orthotitanate and salicylaldehyde; molar ratio 1:2

6.08 g (21.41 mmoles) isopropyl orthotitanate was allowed to react with 5.26 g

(43.11 mmoles) salicylaldehyde in the presence of benzene (10.0 g) at room temperature for 2 h. On drying the product under reduced pressure (1.0 mm) for 3 h a very thick, viscous, yellow liquid (8.95 g) soluble in benzene was obtained. Found: Ti, 11.63%. $(\text{C}_6\text{H}_4\text{O} \cdot \text{CHO})_2 \text{Ti}(\text{OPr}^i)_2$ requires Ti, 11.7%.

The compound $(\text{C}_6\text{H}_4\text{O} \cdot \text{CHO})_2 \text{Ti}(\text{OPr}^i)_2$ develops a characteristic smell and changes to a dirty red solid (A), after a fortnight. 2.0 g compound (A) was redried at room temperature and 1 mm for 4 h. A red residue (1.8 g) was obtained. Found: Ti, 13.6%. 5.0 g of compound (A) was refluxed with 30.0 g benzene for 5 h. The product was dried at 65° and 1.0 mm. A yellowish red solid (4.1 g) was obtained. Found: Ti, 14.6%.

Reaction between isopropyl orthotitanate and salicylaldehyde; molar ratio 1:2

4.64 g (16.30 mmoles) isopropyl orthotitanate reacted with 4.15 g (34.02 mmoles) salicylaldehyde in the presence of benzene (10.0 g) to yield a yellow viscous liquid (6.7 g). Found: Ti, 11.65%. $(\text{C}_6\text{H}_4\text{O} \cdot \text{CHO})_2 \text{Ti}(\text{OPr}^i)_2$ requires Ti, 11.7%.

4.6 g of this compound was dissolved in benzene (50.0 g) and the yellow solution was refluxed for an hour, when its colour changed to red. On refluxing for another 3 h, a red solid began to separate. After concentration, the reaction mixture was allowed to settle. The supernatant red liquor was decanted off and the residue dried at 65° and 1.0 mm. A yellowish red solid (1.9 g) was obtained. Found: Ti, 15.3%.

On standing, the supernatant liquor deposits a red solid which was dried at 65° and 1.0 mm after draining off the liquor. A yellow-orange solid (1.0 g) was obtained. Found: Ti, 16.0%.

Reaction between ethyl orthotitanate and salicylaldehyde; molar ratio 1:2

An exothermic reaction occurred on addition of 7.14 g (58.52 mmoles) salicylaldehyde to 6.73 g (29.52 mmoles) ethyl orthotitanate. The reaction product was dried at room temperature and 1.0 mm for 3 h. Shining light yellow flakes (11.14 g) soluble in benzene were obtained. Found: Ti, 12.6%. $(\text{C}_6\text{H}_4\text{O} \cdot \text{CHO})_2 \text{Ti}(\text{OEt})_2$ requires Ti, 12.6%. 1.4 g of this compound was heated at 100° for an hour and a deep red residue (1.08 g) obtained. Found: Ti, 13.75%.

3.0 g of the compound was refluxed for 12 h with benzene (20.0 g). An orange-red solid (2.0 g) was obtained after decanting off the supernatant red liquor and drying the residue at 60° and 1.0 mm. Found: Ti, 15.85%.

On standing for a fortnight, the compound develops a characteristic odour and becomes an orange red solid (I). 1.2 g was dried at room temperature and 1.0 mm for 4 h. An orange residue (1.16 g) was obtained. Found: Ti, 13.0%.

4.6 g Compound I was refluxed for 4 h with benzene. A red solid (3.5 g) was finally obtained. Found: Ti, 15.7%.

Reaction between isopropyl orthotitanate and salicylaldehyde; molar ratio 1:2 (in refluxing toluene)

Salicylaldehyde (36.92 g, 0.30 mole) was transferred to a solution of 43.0 g (0.15 mole) isopropyl orthotitanate in toluene (125.0 g). On stirring, a yellow solution resulted and noticeable heat was evolved. The reaction mixture was refluxed gently for 2 h at 95°, under the fractionating column. The low boiling fraction (b.p. 57–58°) was with-

drawn very slowly. After collection of nearly 20 ml, over a period of 3 h, the distillate attained a boiling point of 70° . At this stage the fractionation was suspended and the reaction mixture was allowed to reflux for 4 h at 125° when a red precipitate with yellow hue began to separate.

The fractionation was continued until the distillate attained a constant boiling point of $110-5^{\circ}$. Isopropanol and acetone were estimated in both fractions. The reaction mixture was freed of solvent under reduced pressure and then dried at 65° and 1.0 mm. A bright orange-yellow powder (53.8 g) was obtained. Found: isopropanol (in both fractions) 18.5 g; calc. for 2 moles isopropanol (for orthotitanate taken), 18.2 g.

In order to estimate the acetone the weighed sample was added to a solution of 2,4 dinitrophenylhydrazine in sulphuric acid (diluted with 50% ethanol). The mixture was refluxed for 20 minutes and left overnight for crystallisation. The orange-yellow crystals were washed with ethanol, filtered and dried at 50° and 1.0 mm; m.p. 128° . The second fraction contained only traces of acetone. Found: acetone, 9.34 g.

The reaction product (5.07 g; Ti, 13.5%) was heated at 145° and 1.5 mm for 2 h. A yellow residue (4.4 g) was obtained. Found: Ti, 15.3%.

Reaction between tert.-butyl orthotitanate and salicylaldehyde; molar ratio 1:2

3.09 g (9.09 mmoles) *tert.*-butyl orthotitanate reacted with 2.17 g (17.79 mmoles) salicylaldehyde at room temperature, to yield tiny yellow flakes (3.89 g) soluble in benzene. Found: Ti, 10.98%; M. $(C_6H_4O \cdot CHO)_2 Ti(OBu^t)_2$ requires Ti, 10.98%; M.

3.4 g of this compound was refluxed with benzene (20.0 g) for 12 h. The reaction mixture was evaporated to dryness and the product dried at $60^{\circ}/1.0$ mm. A yellow solid (3.4 g) was obtained. Found: Ti, 11.0%.

Action of heat on $(C_6H_4O \cdot CHO)_2 Ti(OBu^t)_2$

$(C_6H_4O \cdot CHO)_2 Ti(OBu^t)_2$, prepared as above, (9.35 g) was heated to 150° and 3.0 mm. A colourless mobile liquid (3.84 g) distilled out, b.p. $92-93^{\circ}/4$ mm. Found: Ti, 14.2%. Calc. for $Ti(OBu^t)_4$: Ti, 14.1%. The distillation was suspended and the residue, a red transparent glass-like mass (4.59 g) gave Ti, 12.2%.

This red residue (3.34 g) was gradually reheated up to $210-215^{\circ}$ at 3.0 mm. A yellow colouration was observed but nothing collected in the receiver. A dark brown fragile voluminous mass (2.77 g) was finally obtained. Found: Ti, 16.3%.

Reaction between titanium tetrachloride and excess salicylaldehyde

Salicylaldehyde (3.40 g, 44.23 mmoles) was transferred to a yellow solution of titanium tetrachloride (2.04 g, 10.74 mmoles) in benzene (40.0 g). An exothermic reaction took place and a chocolate-red precipitate formed, accompanied by brisk evolution of hydrogen chloride. The reaction mixture was allowed to stand for 24 h. It was then refluxed until the evolution of hydrogen chloride became undetectable (18 h). After allowing the reaction mixture to settle, the chocolate-red precipitate was filtered, washed with benzene and dried at $80-85^{\circ}$ at 1.0 mm for 2 h. A dark brown powder (3.5 g), insoluble in benzene, chloroform, dioxane and ethanol was obtained. Found: Ti, 13.4; Cl, 19.4% (Cl:Ti, 1.96:1). $(C_6H_4O \cdot CHO)_2 TiCl_2$, requires Ti, 13.3; Ti, 13.3; Cl, 19.7%.

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A REACTION RATE STUDY IN HYDROFLUORIC ACID OF THE DISSOLUTION OF TITANIUM AND THE ALPHA SOLID SOLUTION OF OXYGEN IN TITANIUM

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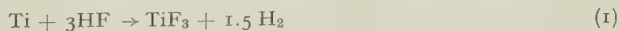
SUMMARY

Studies were conducted into the mechanism of dissolution in hydrofluoric-hydrochloric acid mixtures of titanium and of alpha solid solution specimens of oxygen in titanium. Special precautions were taken to preserve the trivalent state of titanium. For titanium a rate order of 0.76 and an activation energy of 6.9 ± 0.5 kcal was found and for titanium in TiO_x a rate order of 0.83 and an activation energy of 6.6 ± 0.5 kcal. Furthermore, the oxygen content of TiO_x , within the range studied, had no effect on the rate of hydrogen evolution; all specimens evolved hydrogen at the same fixed rate per unit area for a given temperature. It is concluded that a diffusionaly controlled reaction can best explain the results.

INTRODUCTION

A review of the literature¹⁻³ involving the dissolution of titanium in hydrofluoric acid suggested that a further investigation into the subject might provide a better understanding of the mechanism. Accordingly, rate studies were carried out on the dissolution in hydrofluoric-hydrochloric acid mixtures of titanium and solid solutions of oxygen in titanium to determine whether the kinetics of the latter were vastly different from those of the metal.

The TiO_x specimens to be studied lay in the alpha solid solution region of the Ti-rich portion of the constitution diagram for Ti-O⁴. From previous work⁵ it was concluded that TiO_x was a solid solution of Ti and Ti_2O_3 . This suggested that only free titanium, *i.e.*, that not bonded with oxygen evolved hydrogen



the Ti_2O_3 dissolving with no hydrogen evolution. From these facts one might expect the kinetics for Ti in TiO_x and titanium sheet in HF to be the same, thus affording an insight into the probable mechanism for titanium dissolution.

EXPERIMENTAL

Material and apparatus

A specimen of commercial grade titanium metal was cut from a sheet of cold rolled metal (stress-relieved by annealing) and mounted in clear lucite plastic attached

to a stirrer so as to expose 1 cm^2 of surface to the acid. Prior to dissolution all samples were ground, polished, and etched in 3 N HF .

The apparatus used is described in the literature². To preserve the trivalent state of titanium, all oxygen in the system prior to each experiment was eliminated by flushing the apparatus with pure hydrogen gas. This was necessary since any oxygen remaining would tend to enter into an oxidation reaction which might alter the volume of H_2 collected per dissolution experiment. A volume of 300 ml of acid was used in all experiments and the temperature was controlled within $\pm 0.1^\circ\text{C}$.

The Ti-O alloys were prepared by thoroughly mixing calculated amounts of titanium powder (65 mesh, 98.27% pure, the balance being mainly oxygen) and titanium dioxide (reagent grade, 99.9% pure), and compacting the mixture in a 1-in. diam. die under a pressure of 7 t.s.i. The powder specimens were transferred to an alundum crucible and sintered in a vacuum resistance furnace for a period of 4 h at 1400°C (vacuum 2-3 microns). At the end of the reaction period the reaction tube was sealed off, air-quenched and allowed to stand overnight. The thoroughly sintered specimen was removed from the furnace, the higher oxide layer scraped from the surface, and the sample examined microscopically to determine homogeneity. The samples were then cut to size, polished and mounted in the same manner as described for titanium metal.

Analyses of the Ti-O samples were made using the hydrogen evolution method⁵. Four specimens were prepared within the alpha solid solution region (4.50 to 14.0% oxygen at 1400°C) corresponding to 4.97, 7.02, 7.98, and 10.8% oxygen b.w.

RESULTS

Rates with Ti metal

Since the velocity of the liquid across the sample surface affects the rate of dissolution, the influence of stirrer speed was observed for titanium dissolving in 0.10 N HF – 1.0 N HCl at 25.0°C . The rate of hydrogen evolution for the range 0–460 rev/min is given by the plot of V versus s (Fig. 1), where V is the rate in units of $\text{mm}^3\text{cm}^{-2} \text{ min}^{-1}$ (eqn. 2) and s is the stirrer speed in rev/min. A stirrer speed of 200 rev/min was maintained throughout all experiments. The maximum rates observed in each experiment are shown in Fig. 1.

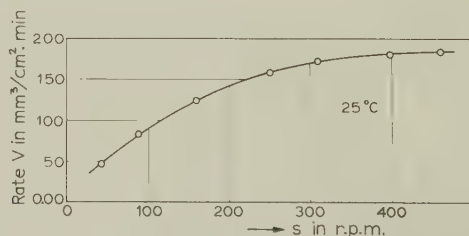


Fig. 1. Rate of hydrogen evolution V as a function of stirrer speed in rev/min. Titanium dissolving in 0.1 N HF , 1 N HCl .

These rates were calculated using the expression

$$V = \frac{1000 \Delta v}{A \Delta t} \text{ mm}^3\text{cm}^{-2}\text{min}^{-1} \quad (2)$$

where Δv is the volume of H₂ in ml at STP evolved in Δt minutes and A is the area of the sample in cm².

From the stoichiometry of eqn. 1 the rate may be expressed in mg of Ti cm⁻²mm⁻¹ by multiplying eqn. 2 by the factor

$$\frac{2 \times 47.9}{3 \times 22,414} = 0.001425$$

The dissolution of titanium at four concentrations of HF, 0.050, 0.075, 0.10, and 0.50 *N*, all 1.00 *N* with respect to HCl, and at temperatures of 15°–45°C was investigated. Hydrochloric acid was added to control the equilibrium concentration of fluoride complexes. The concentration of the un-ionized HF was therefore essentially the same as the stoichiometric concentration of the acid. From plots of $\ln(\text{rate})$ versus $\ln(\text{acid})$ concentration an order of 0.76 was obtained. Hence, the rate of dissolution obeys the equation

$$V = kC^{0.76} \quad (3)$$

where k is the reaction rate constant in mm³cm⁻²mm⁻¹ liters equiv.⁻¹, and C the equiv. liter⁻¹ of the acid.

Similar results ($V = kC^{0.81}$) were obtained within error limits for the order of dissolution of titanium in HF in the absence of HCl. The rates of hydrogen evolution were higher, however, in the HF–HCl mixtures owing to the shift in equilibrium toward higher concentrations of un-ionized HF, although the increase could not be entirely accounted for by the equilibrium constant⁶. The rates were therefore dependent upon un-ionized HF as observed in experiments with other metals dissolving in HF^{7,8}.

Rates with TiO_x solid solutions

The dissolution of the four solid solution specimens was conducted at 25.0°C and in four hydrofluoric acid concentrations of 0.050, 0.075, 0.10 and 0.50 *N* all 1.00 *N* with respect to HCl. From a plot of $\ln(\text{rate})$ vs. $\ln(\text{concentration})$ the rate equation obtained for the dissolution of the Ti not bonded with oxygen in TiO_x is

$$V = kC^{0.83} \quad (4)$$

Table I summarizes the results for the four samples of TiO_x.

An examination of Table I reveals that the rate of hydrogen evolution for all of the specimens at a given acid concentration is nearly constant. Attempts to prepare specimens of lower oxygen content were not successful. The scatter from one specimen to another suggests no real differences. On this basis the average rate of hydrogen evolution was calculated for each acid concentration and is shown in Table I.

The total rate of dissolution of TiO_x in mg cm⁻² min⁻¹ was then determined from the established stoichiometry of eqn. 5,

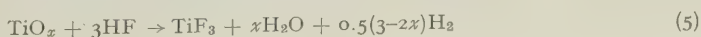


TABLE I
SUMMARY OF DISSOLUTION RATES OF THE Ti-O ALPHA SOLID SOLUTION IN HF-HCl
MIXTURES AT 25.0°C
(Conc. of HCl, 1 N throughout)

Sample	Rates of H_2 evolution* ($mm^3cm^{-2}min^{-1}$) in HF			
	HF Normality			
	0.05	0.075	0.1	0.5
TiO _{0.157}	102	164	248	924
TiO _{0.226}	89	157	210	715
TiO _{0.260}	118	175	193	618
TiO _{0.365}	100	204	246	775
Average	102	175	224	758

* Each rate value an average of two runs.

and is summarized in Table II.

TABLE II
TOTAL RATES OF DISSOLUTION ($mgcm^{-2}min^{-1}$) OF TiO_x ALLOYS IN
VARYING HF CONCENTRATIONS AT 25.0°C

Sample	HF Normality			
	0.050	0.075	0.10	0.50
TiO _{0.157}	0.171	0.293	0.375	1.27
TiO _{0.226}	0.184	0.316	0.404	1.37
TiO _{0.260}	0.191	0.328	0.420	1.42
TiO _{0.365}	0.216	0.370	0.474	1.60

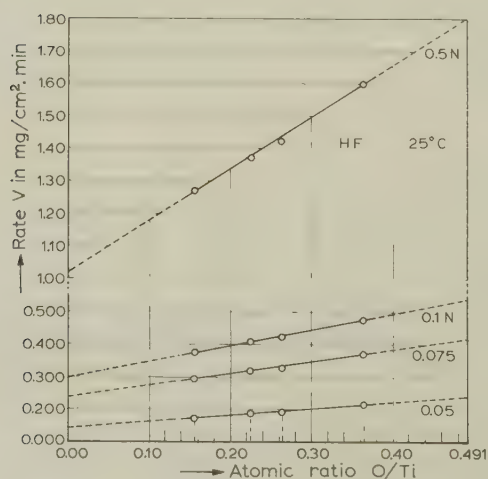


Fig. 2. Total rate of dissolution of TiO_x alloys (α -phase border at 14.0% b.w. of O) in a mixture of 0.10 N HF and 1.00 N HCl.

The variation of dissolution of the alpha solid solutions in 0.10 *N* HF–1.00 *N* HCl with respect to the atomic ratio (O/Ti) is shown in Fig. 2. The straight lines are extrapolated in both directions so as to cover the entire alpha solid solution region. The extrapolated values of the rate at 0.000 (O/Ti) are 0.140, 0.235, 0.296 and 1.019 as compared to respective values of 0.110, 0.157, 0.210 and 0.656 mgcm⁻²min⁻¹ for the commercial metal. The larger values for the powder metallurgy products are expected since the surface area on a micro scale is undoubtedly larger than for the solid metal. Nevertheless, the reaction order, calculated from the rate values extrapolated to zero oxygen, agrees within the limits of error with that obtained for the compact metal (0.77 *vs.* 0.76).

Effect of temperature on rates

Rate studies were made on both titanium metal and TiO_x alpha solid solutions dissolving in 0.10 *N* HF–1.00 *N* HCl over a range of temperatures that included 15, 25, 35 and 45°C. From the average maximum rates the reaction rate constants were obtained and graphs of $\ln k$ *vs.* $1/T$ were constructed. A straight line was obtained in each case as expressed by the following equations; and the activation energies E_a^* were calculated

$$\begin{aligned}\ln k &= -3.50 \cdot 10^3/T + 18.5 \text{ (Ti)} \\ E_a^* &= 6.93 \text{ kcal}\end{aligned}\tag{6}$$

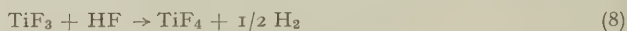
$$\begin{aligned}\ln k &= -3.33 \cdot 10^3/T + 18.5 \text{ (Ti in TiO}_x\text{)} \\ E_a^* &= 6.63 \text{ kcal}\end{aligned}\tag{7}$$

DISCUSSION AND CONCLUSIONS

From the relatively low values of the temperature coefficient (E_a^*) and the stirring effect, the slow step is suggested to be physical rather than chemical. However, chemical activation steps cannot be excluded on the basis of energy magnitude alone, particularly if electrochemical processes are involved.

If the dissolution is controlled by a chemical activation step it is difficult to explain the experimental evidence establishing within error limits a fixed rate of hydrogen evolution per unit area of TiO_x specimens in the same acid concentrations. These results appear to favor the physical activation step since one would expect that the presence of varying amounts of Ti₂O₃ (incapable of producing hydrogen) as cathodic sites would have a decided effect on the rate of hydrogen evolution of titanium not bonded with oxygen, particularly if an electrochemical mechanism were rate-controlling. Furthermore, the reaction orders and activation energies for titanium sheet and Ti in TiO_x dissolving in HF are equal within experimental limits of error, indicating that varying amounts of the oxide cause no measurable difference in the kinetic properties of the two titanium samples. If the reaction is diffusionaly controlled and obeys Fick's first law the rates should be proportional to the HF concentration, yielding an order of one as observed for other metals dissolving in HF⁶⁻⁹. The deviation of the value from unity cannot be attributed to experimental technique since run after run has resulted in values always close to 0.80 and the methods are the same as used for zirconium and hafnium studies^{8,9}.

It is known that a very slow reaction of TiF_3 with HF results in hydrogen evolution according to the equation



If one assumes that the process of dissolution of Ti involves competition of a product TiF_3 for the diffusing molecular HF according to the following equations



this may account, since reaction 8 is very slow, for the experimental order being less than unity¹⁰. Further experiments are in progress to account for the observed order.

From the foregoing it can be concluded that the slow step cannot be electrochemically controlled and that since the order and activation energy for the dissolution of titanium metal and Ti in TiO_x in HF are the same, the mechanism of dissolution is the same for both; the slow step is probably governed by the diffusion of molecular HF to the reacting surface.

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THE CONSTITUTION DIAGRAM OF THE TUNGSTEN-OSMIUM BINARY SYSTEM

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SUMMARY

The constitution diagram of the refractory alloy binary system tungsten-osmium has been determined using a combination of X-ray and micrographic techniques. The system contains three single-phase fields, namely:

(a) a body-centered cubic α -W primary solid solution which retains approximately 18.5 at. % Os at the peritectic temperature of 2945°C, dropping to approximately 6 at. % Os at 1200°C;

(b) a tetragonal σ -phase which forms peritectically at 22 at. % Os and at a temperature of 2945°C by reaction between α -W solid solution and liquid, the σ -phase field opening out and extending at 1200°C from 21 to 35 at. % Os;

(c) a hexagonal close-packed terminal solid solution based on θ -Os, whose solid solubility limit ranges from 46 at. % Os at the eutectic temperature of 2725°C to 68 at. % Os at 1200°C.

Lattice parameters have been evaluated for α -, σ -, and θ -phase alloys along with their Vickers hardness values. Sigma-phase alloys have been found to be extremely hard and brittle and scratch glass very easily.

INTRODUCTION

Very little detailed information concerning the tungsten-osmium system was available prior to the present investigation, the only previous study having been made by RAUB AND WALTER^{1,2} using alloys of unspecified purity prepared for them by the Heraeus Company, the method of production not being stated. No attempt was made in that investigation to determine either the solidus and liquidus curves or the solid-solubility limits over a range of temperatures. Their investigation, based on alloys annealed at 1800°C, revealed three single-phase fields, namely the α -W primary solid solution containing up to 5 at. % osmium, an intermetallic compound having the stoichiometric composition of W_3Os , the X-ray data being subsequently interpreted by PEARSON³ as corresponding to a σ -phase alloy having the β -U structure, and, finally, their investigation revealed a θ -phase ranging from approximately 52 at. % osmium to pure osmium.

In the present investigation, the findings of which confirm and extend those of RAUB AND WALTER, special melting, heat-treatment and X-ray specimen preparation

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techniques were evolved to overcome the difficulties associated with the easily oxidizable nature of the alloying elements and their alloys in addition to the problems encountered in the production of uniform specimens on account of the unusually high homogenizing temperatures required.

EXPERIMENTAL

(a) *Materials*

The alloying elements were of the highest obtainable purity. The tungsten was specially prepared for the investigation by the Westinghouse Lamp Division at Bloomfield. It was supplied in the form of lightly sintered bar of approximately $\frac{1}{2}$ in. square section, the material being easily broken into small pieces or crushed to fine powder. The impurities in parts per million (by weight) were 20 Fe, 10 Al, 10–20 Si, 10 Mg + Cu, 10 Ni, 10–20 Mo, 5 O₂, 5 N₂, 20–40 C. The osmium, which was supplied by BAKER in the form of sponge, had a purity of approximately 99.99% with no N₂, C not detected, and negligible O₂.

(b) *Heat treatment*

Alloy preparation, homogenization, and equilibrating heat treatments of ingot and powder samples have been described in a previous paper along with the temperature-measuring techniques⁴. In brief, the alloys were melted in the form of 30 g buttons in purified argon using a Kroll type arc furnace fitted with a non-consumable tungsten electrode and a water-cooled copper hearth. Long period homogenization anneals on the lump samples were carried out in an evacuated high frequency furnace fitted with a tungsten susceptor, while melting point determinations and short-term heat treatments immediately below the solidus were effected using a directly heated vertical tungsten tube furnace, the alloys being quenched into molten tin. Temperatures were measured under near black-body conditions using a Leeds and Northrup disappearing filament optical pyrometer calibrated at the National Bureau of Standards, a correction being applied for emissivity and reflections from the surfaces of the fused quartz sight glasses covering the furnace observation ports.

(c) *Alloy composition*

Except for a few of the σ -phase alloys, the compositions of which were checked by X-ray fluorescence analysis, the weight losses sustained during the melting process and subsequent heat treatments were so small, and the X-ray and micrographic results so self-consistent, that little would have been gained by chemical analysis. However, when annealing for prolonged periods under vacuum at temperatures in the vicinity of the solidus, it was found that slight weight losses were sustained which micrographic examination indicated to be confined to a sharply delineated surface layer which was, at most, only a few thousandths of an inch in thickness. This impoverished layer was always removed before preparing powder samples for X-ray diffraction analysis, thus ensuring X-ray results which were truly representative of the nominal weighed-out compositions.

(d) *Preparation of micro specimens*

All specimens were polished on automatic machines, the procedure being to grind on silicon carbide papers, rough polish to 6 μ diamond, and finish on Linde B (0.2 μ

sapphire dust)*. The samples were then etched electrolytically in the following solutions:

(1) *Tungsten etch*

H ₂ O	150
K ₃ Fe(CH) ₆	3.5
KOH	1

(2) *Acetic acid etch*

Acetic acid	75
HNO ₃	25
HF	2

(3) *Peroxide etch*

H₂O₂ (30%) cold, or
H₂O₂ (3%) boiling

(e) *X-Ray techniques and sample preparation*

Diffraction patterns of powdered alloys were taken in a Philip's 114.6 mm diameter Debye-Scherrer camera using a high-intensity rotating-anode demountable X-ray tube⁵. Although cobalt $K\alpha$ radiation proved to be eminently satisfactory for phase identification throughout the system it proved suitable only for lattice parameter determinations of alloys in the body-centered cubic α -W field. The complex nature of the diffraction patterns from the tetragonal alloys in the σ -phase field necessitated the use of chromium $K\alpha$ radiation to achieve higher resolution and to enable the high-angle reflexions to be correctly indexed for parameter determination. Finally, hexagonal close-packed alloys in the θ -Os-phase field were re-photographed with zinc $K\alpha$ radiation in order to place the sensitive 0006 reflection at a Bragg angle in the region of 83° (*cf.* Fig. 11). The final parameters were obtained by extrapolating the observed spacings against the function $1/2(\cos^2 \theta/\theta + \cos^2 \theta \sin \theta)$ ^{6,7}, the precision obtained being about one part in 30,000. Alloys in the σ -phase field, after heat treating the lump sample, could be examined in the "as-crushed" condition without appreciable line-broadening on account of their extremely brittle nature, but similarly crushed alloys in the α -W and θ -Os-phase fields required a low temperature "flash" recovery anneal prior to X-raying, as described in a previous publication⁴.

THE TUNGSTEN-OSMIUM SYSTEM

The single-phase fields of the tungsten-osmium system consist essentially of:

- (1) the body-centered-cubic α -W primary solid-solution.
- (2) the σ -phase field, alloys of which have the tetragonal β -U type of atomic arrangement.
- (3) the hexagonal close-packed θ -Os terminal primary solid-solution.

(a) *The α -W phase field*

As shown by the constitution diagram in Fig. 1, the α -W phase field extends from pure tungsten to 18.5 at. % osmium at 2945°C, narrowing down to approximately

* The authors wish to thank Mr. ROY ANDERSON for the metallographic preparation of samples.

6 at. % osmium at 1200°C. The solid solubility limits above 2200°C were determined by micrographic examination, while the limits at 2200°C, 1500°, and 1200°C were derived from lattice parameter measurements on quenched alloys, the results being confirmed micrographically.

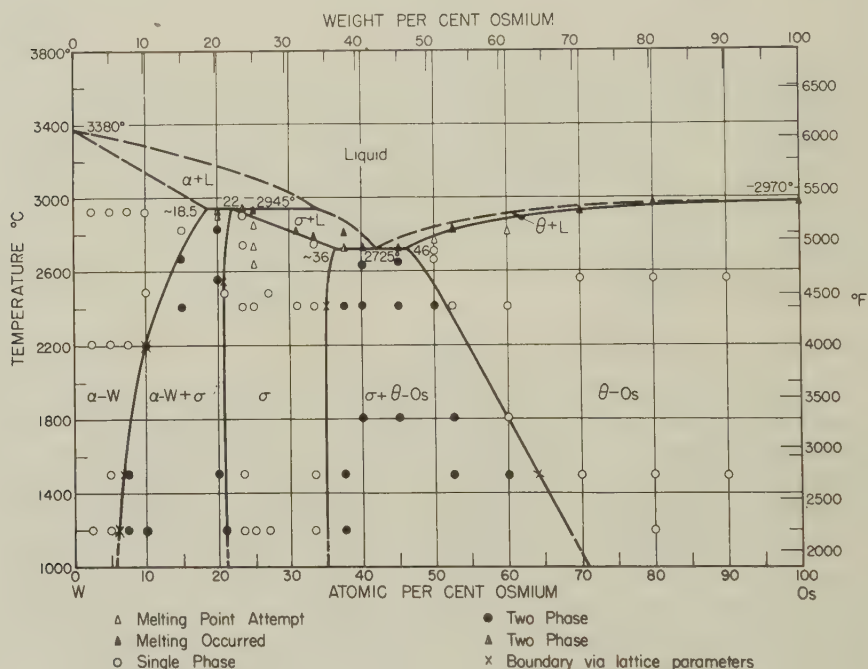


Fig. 1. The tungsten-osmium system.

The lattice parameters of alloys as a function of composition are shown plotted in Fig. 2 for the α -W phase field. As would be expected from a consideration of the atomic radii of the alloying elements, the addition of osmium reduces the lattice parameter of tungsten. The rate of change is relatively small however, 10 at. % of osmium reducing the tungsten parameter by 0.27%. The change with composition is non-linear, the curve being slightly concave upwards.

The addition of osmium increases the Vickers hardness of tungsten, the hardness number increasing from 383 for pure tungsten to 500 for an α -W phase alloy containing 7.5 at. % osmium. These results are summarized in Table I along with details of heat treatment, observed structures and X-ray data.

(b) The σ -phase field

The σ -phase forms peritectically at 22 at. % osmium at a temperature of 2945°C, the reaction which takes place occurring between liquid (containing approximately 34 at. % osmium) and α -W solid solution (18.5 at. % osmium). The phase field broadens out from the peritectic point at 22 to 21 at. % osmium at 2200°C at the tungsten-rich boundary and to 35 at. % at the osmium-rich boundary. As would be expected, the lattice parameters of the tetragonal unit cell fall continuously with the replace-

TABLE I
SUMMARIZED DATA ON TUNGSTEN-OSMIUM ALLOYS

Alloy number	Osmium atomic %	Melting point (°C)	Heat treatment** (°C)	Observed structure	Lattice parameter (Å)	Atomic volume (Å ³)	Vickers hardness
—	0.0	3380		α	3.16496	15.8511	371
8	2.5		2928° 41 h + 2211° 16 h + 1200° 27 days	α α α	3.16224	15.8108	416
9	5.0		2928° 41 h + 2211° 16 h + 1503° 161 h + 1200° 27 days	α α α α	3.16028	15.7814	516
10	7.5		2928° 41 h + 2211° 16 h + 1503° 161 h + 1200° 27 days	α α α α + σ	3.1582 ₉ 3.1591	15.7516	681
11	10.0		2928° 41 h + 2488° 4 h + 2211° 16 h + 1200° 27 days	α α α + σ α + σ	3.1572 ₀ 3.1571 ₅ 3.1594	15.7353	723
15	15.0		2416° 55 h + 2826° 2 h + 2675° 2 h	α + σ α α + σ			
2	20.0		2559° 48 h + 2935° 5 min + 2903° 5 min + 2837° 52 min + 1503° 161 h + 1200° 27 days	α + σ α + σ α + σ α + σ α + σ α + σ	$a = 9.6714$ $c = 5.0158$ $c/a = 0.51862$	15.6386	910

TABLE I (Continued)

Alloy number	Osmium atomic %	Melting point (°C)	Heat treatment** (°C)	Observed structure	Lattice parameter (Å)	Atomic volume (Å ³)	Vickers hardness
21	21.0		2483° 19 h + 1200° 27 days	σ $\alpha + \sigma$	$a = 9.6685$ $c = 5.0135$ $c/a = 0.51853$	15.6220	
16	23.5*	2935°	2416° 73 h + 2905° 15 min + 2743° 3 h + 1500° 161 h + 1200° 27 days	σ σ σ σ σ	$a = 9.6640$ $c = 5.0090$ $c/a = 0.51831$	15.5935	
3	25.0	2935°	2416° 50 h + 2852° 5 min + 2735° 5 min + 2637° 5 min + 1200° 27 days	σ σ σ σ σ	$a = 9.6630$ $c = 5.0068$ $c/a = 0.51814$	15.5834	1789
20	27.0*		2483° 19 h + 1200° 27 days	σ σ	$a = 9.6590$ $c = 5.0010$ $c/a = 0.51775$	15.5525	
4	31.0*	2821°	2416° 50 h	σ	$a = 9.6463$ $c = 4.9889$ $c/a = 0.51718$	15.4741	1736
5	33.3*	2796°	2416° 50 h + 2750° 5 min + 1503° 151 h + 1200° 27 days	σ σ σ σ	$a = 9.6343$ $c = 4.9810$ $c/a = 0.51700$	15.4112	1689

TABLE I (Continued)

Alloy number	Osmium atomic %	Melting point (°C)	Heat treatment** (°C)	Observed structure	Lattice parameter (Å)	Atomic volume (Å ³)	Vickers hardness
17 b	37.5	2816°	2416° 57 h + 2725° 5 min + 1503° 161 h + 1200° 27 days	$\sigma + \theta$ $\sigma + \theta$ $\sigma + \theta$ $\sigma + \theta$	$a = 9.6254$ $c = 4.9765$ $c/a = 0.51700$	15,3688	1590
6	40.0	2723°	2416° 50 h + 2635° 5 min + 1804° 72 h	$\sigma + \theta$ $\sigma + \theta$ $\sigma + \theta$			1431
18 b	45.0	2723°	2416° 55 h + 2052° 1 h + 1804° 72 h	$\sigma + \theta$ $\sigma + \theta$ $\sigma + \theta$			
7	50.0		2416° 50 h + 2765° 5 min + 2713° 5 min + 2665° 2 h	$\theta + \sigma$ θ θ θ			650
19 b	52.5	2826°	2416° 55 h + 1800° 72 h + 1499° 15 min***	θ $\theta + \sigma$ $\theta + \sigma$			568
11	60.0		2416° 50 h + 2816° 5 min + 1804° 72 h + 1499° 15 min***	θ θ θ $\theta + \sigma$	$a = 2.7655$ $c = 4.4498$ $c/a = 1.6090$	14,7363	
12	70.0	2923°	As-cast 2450° 48 h + 1499° 15 min***	θ θ	$a = 2.7619$ $c = 4.4083$ $c/a = 1.5961$	14,5609	823

TABLE I (Continued)

Alloy number	Osmium atomic %	Melting point (°C)	Heat treatment** (°C)	Observed structure	Lattice parameter (Å)	Atomic volume (Å ³)	Vickers hardness
13	80	2970°	As-cast	θ	$a = 2.7533$ $c = 4.3706$ $c/a = 1.5874$	14.3466	798
			2560° 48 h				
			+ 1499° 15 min***				
14	90.0	2970°	+ 1200° 27 days	θ	$a = 2.7437$ $c = 4.3418$ $c/a = 1.5825$	14.1528	742
			As-cast				
			2560° 48 h				
—	100	2970°	+ 1499° 15 min***	θ -Os	$a = 2.7341$ $c = 4.3199$ $c/a = 1.5800$	13.9831	530
			As-cast				
			1499° 15 min***				

* Checked by X-ray fluorescence analysis.

** First entry is original homogenizing anneal.

*** Powder anneal only, after high-temperature homogenization of ingot.

ment of tungsten by osmium, the axial ratio reaching a constant value of 0.502 a little before the osmium-rich boundary is reached (*cf.* Table I). The lattice parameters and axial ratios are shown plotted against composition in Fig. 3, the compositions being checked by fluorescence analysis.

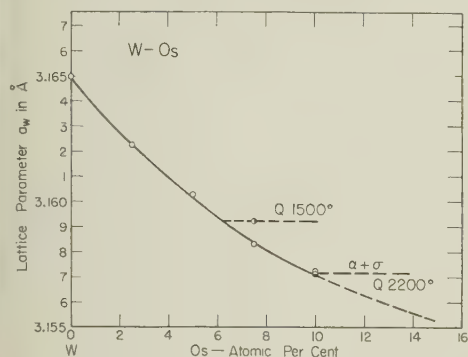


Fig. 2. Lattice parameters of α -phase W-Os alloys.

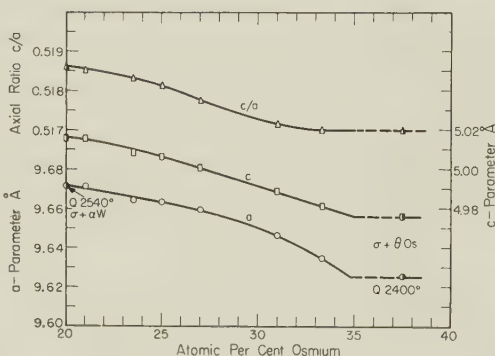


Fig. 3. Lattice parameters of σ -phase W-Os alloys.

Alloys in the σ -phase field are extremely hard and brittle, their Vickers diamond micro-hardness numbers being of the order of 1700 (*cf.* Table I). These alloys scratch glass very easily. They also become superconductors as the absolute zero is approached⁸.

(c) The θ -Os phase field

As may be seen from Fig. 1, the phase field occupied by the hexagonal close-packed θ -Os terminal solid solution is extremely wide. The solid solubility limit of the phase lies at 46 at. % osmium, the temperature, 2725°C, being that of the eutectic which occurs at approximately 42 at. % osmium by reaction between σ - and θ -Os. The θ -Os phase narrows down with falling temperature, the solid solubility limit changing from 46 at. % osmium at the eutectic temperature to 64 at. % osmium at 1500°C, the limit at the higher temperature being obtained by combined X-ray and micrographic examination, while the low temperature limit is finally set by lattice parameter determinations. Lattice parameter results are collected in Table I and are shown plotted in Fig. 4. Again, as expected, the lattice parameters fall with increasing osmium content, while the axial ratio which has a value of 1.609 at 65 at. % osmium falls steadily to a value of 1.580 for pure osmium. The Vickers hardness of θ -Os alloys drops from 650 at 50 at. % Os to 530 for the pure element. Single-phase θ -Os alloys near the θ -Os/ $\sigma + \theta$ boundary are very tough but also scratch glass very easily.

ATOMIC VOLUMES OF THE PHASE STRUCTURES

Figures 2, 3 and 4 show a continuous fall in lattice parameters with increasing osmium content irrespective of phase structure. To place the results on a comparative basis, Fig. 5 illustrates the changes in atomic volume which occur with composition assuming 2 atoms per unit cell in the body-centered cubic α -W phase structure, 30 atoms per unit cell in the tetragonal σ -phase and 2 atoms per unit cell in the close-packed hexagonal unit. Almost the same shape of curve is obtained if we plot ρ^3/V instead.

As may be seen there is a marked positive deviation from an additivity law in both the α -W and σ -phases. In the θ -Os phase field, there is a positive deviation in the vicinity of the phase boundary at 65 at. % Os, but this becomes very slightly negative

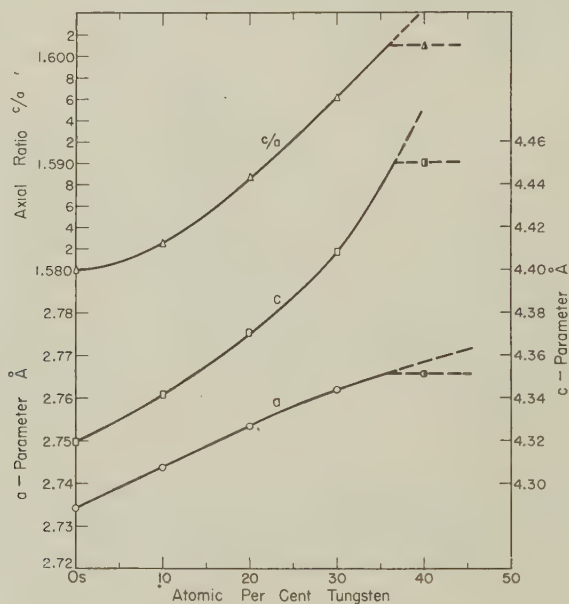


Fig. 4. Lattice parameters and axial ratios *versus* composition for θ -phase tungsten-osmium alloys. Powders annealed at 1500°C and radiation quenched.

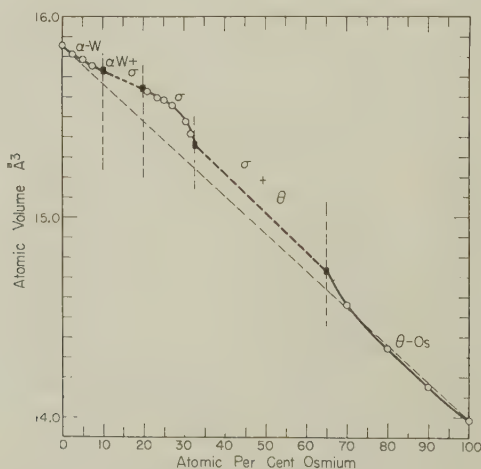


Fig. 5. Atomic volumes of W-Os alloys. ○, Single-phase alloys; ■, atomic volume at phase boundary based on alloys in the two-phase field.

in the central portion of the phase field around 80-90 at. % osmium. These atomic volume relationships are rather unusual, the normal tendency being for a marked contraction in atomic volume to occur in the intermediate phases of alloy systems as well as in their primary and terminal solid solutions⁹.

MICRO-STRUCTURES AND X-RAY DIFFRACTION PATTERNS

Photomicrographs of a 45 at. % osmium alloy in the as-cast condition and after annealing at 2800°C are shown in Figs. 6 and 7. The as-cast structure consists of a $\sigma + \theta$ eutectic in a matrix of θ -Os primary solid solution. The annealed structure consists essentially of $\sigma + \theta$ -Os. Figs. 8, 9 and 10 illustrate the effects of heat treatment on the microstructure of a 50/50 tungsten-osmium alloy and reveal the formation of a single-phase θ -Os structure at 2680° followed by its decomposition into $\sigma + \theta$ at 2400°C.

X-ray patterns typical of the various phase fields are shown in Fig. 11. The sharpness of the high order reflections indicates the homogeneity of the alloys. The θ -Os diffraction patterns are taken with Zn $K\alpha$ radiation to obtain a 0006 reflection at a Bragg angle lying above 80° in order to obtain accurate values of the c -parameters. The large movement of the high order reflections in the σ -phase patterns is also much in evidence and indicates a parameter drop of about 1% in crossing the single-phase field in the direction of higher osmium.

In their work on the tungsten-rhenium system, DICKINSON AND RICHARDSON¹⁰ report the presence of a χ phase at Re_3W having the α -magnetic structure. This χ phase is formed via a peritectoid reaction at 2125°C between σ -phase (containing 69 at. % Re) and hexagonal close-packed Re solid solution (containing 73 at. % Re). The formation of an analogous χ -phase was sought in the tungsten-osmium system but no signs of its occurrence could be detected.

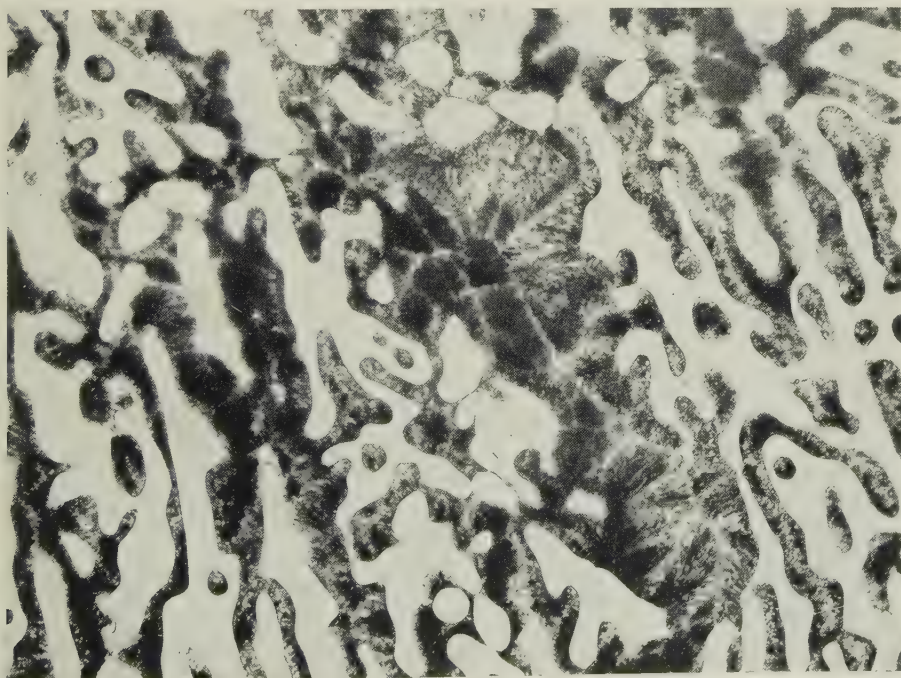


Fig. 6. Photomicrograph of W-Os-18, W55 Os45 at.%. As-cast. ($\theta +$ eutectic). $\times 200$

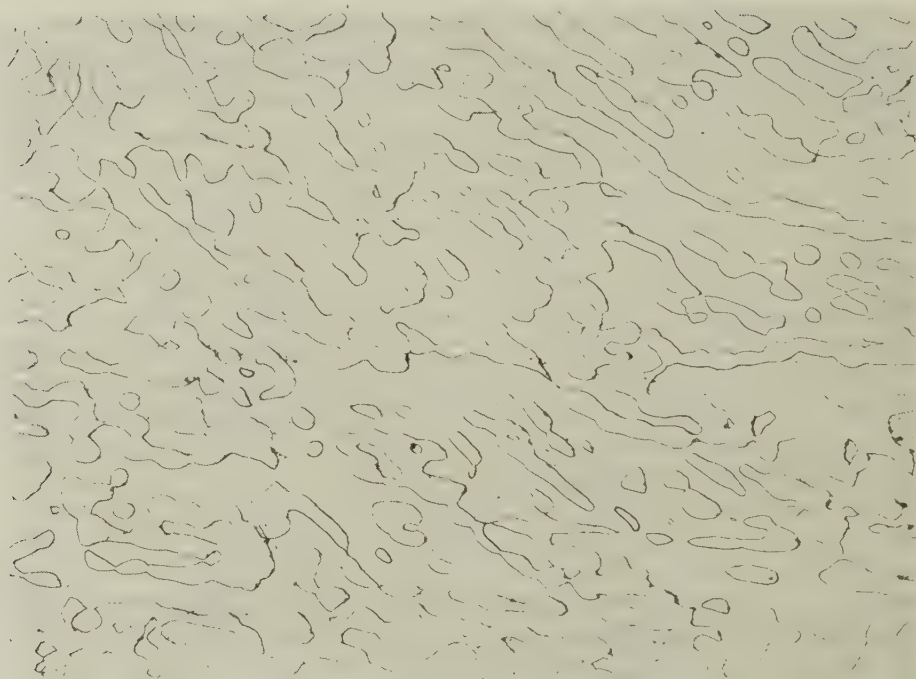


Fig. 7. Photomicrograph of W-Os-18, W55 Os45 at. %. Lump annealed 50 h at 2400°C. Radiation quenched. $\times 200$

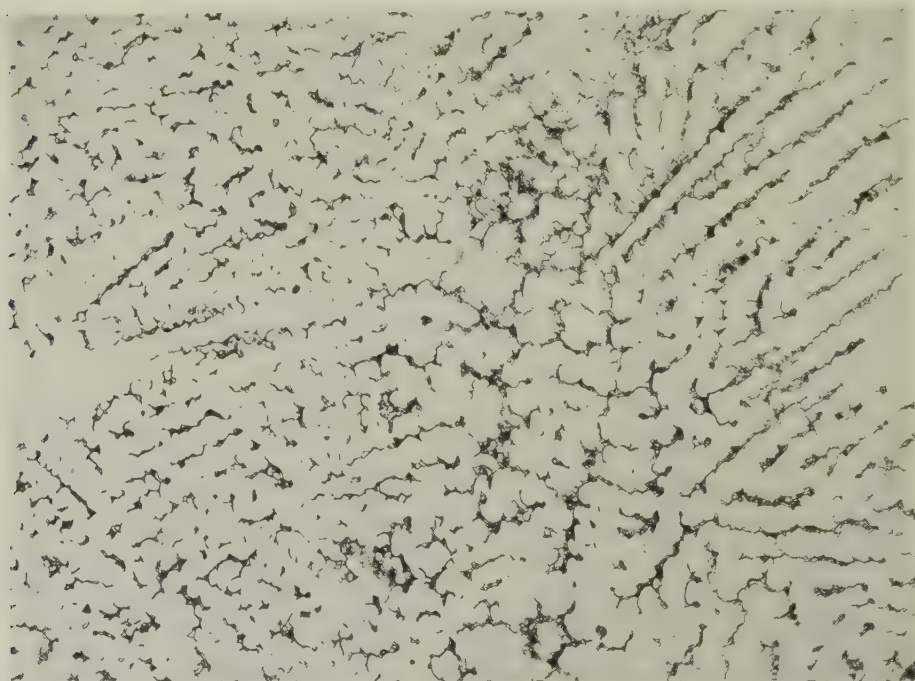


Fig. 8. Photomicrograph of W-Os-7, W50 Os50 at. %. As-cast (θ + eutectic). $\times 200$



Fig. 9. Photomicrograph of W-Os-7, W₅₀ Os₅₀ at. %. Lump annealed 2 h at 2680°C. Radiation quenched. $\times 200$

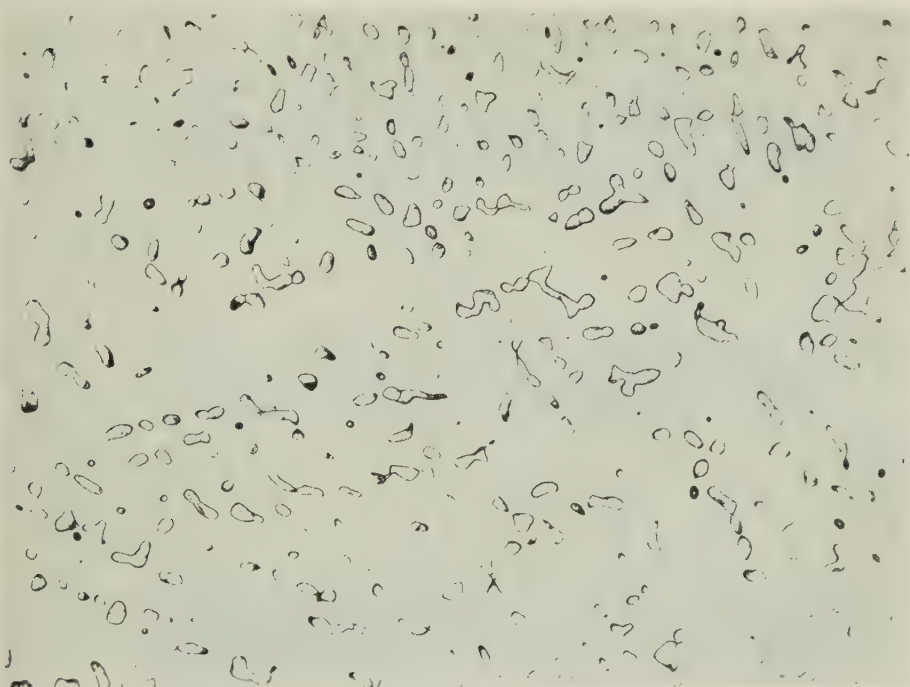


Fig. 10. Photomicrograph of W-Os-7, W₅₀ Os₅₀ at. %. Lump annealed 50 h at 2400°C. Radiation quenched. $\times 200$

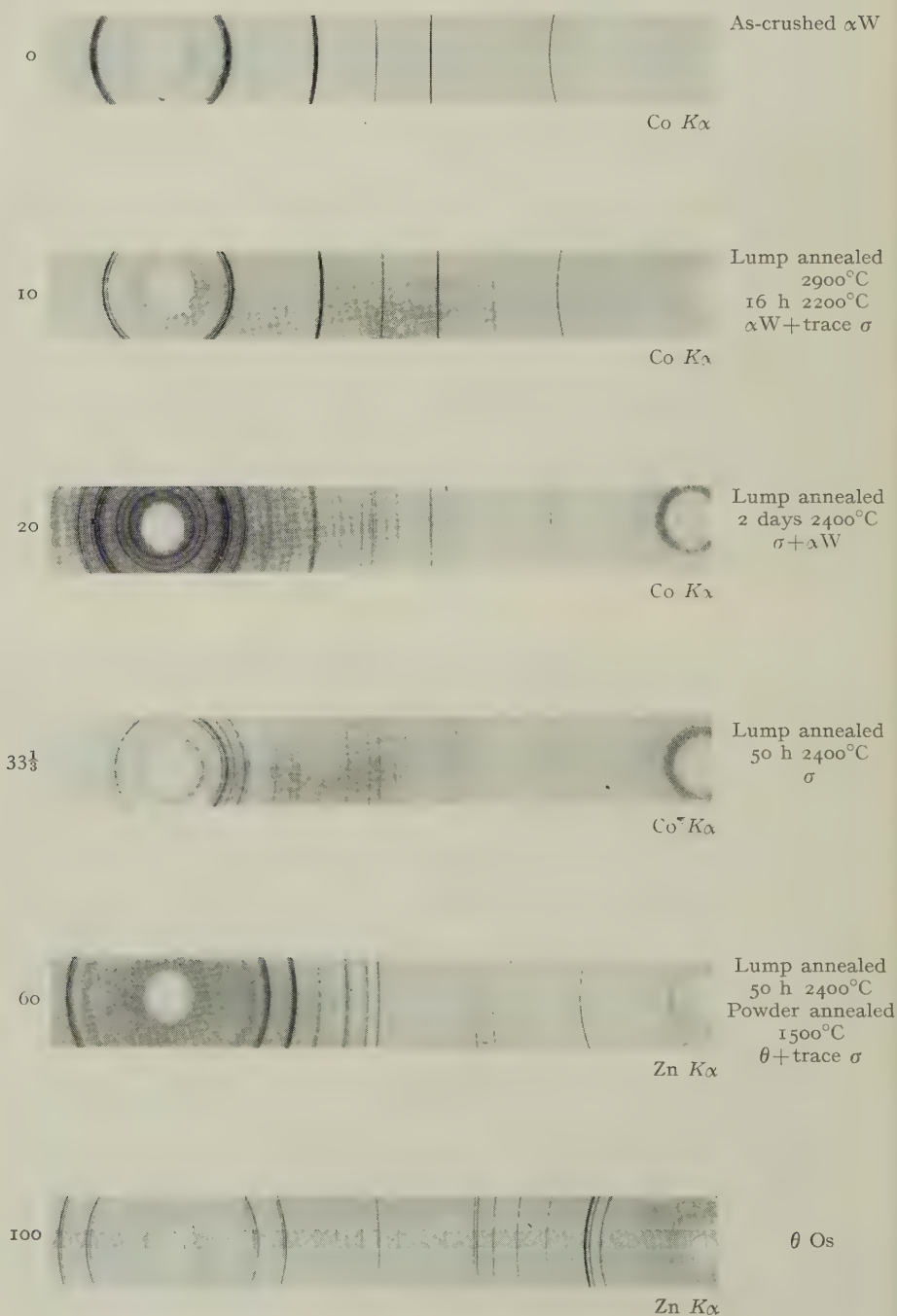
Atomic
% Os

Fig. 11. X-ray diffraction patterns of tungsten-osmium alloys.

THE MELTING POINT OF OSMIUM

The melting point of all alloys on the tungsten-rich side of the eutectic horizontal were made in the tungsten tube furnace with the specimens suspended directly on a thin tungsten wire. In the case of the osmium-rich tungsten-osmium alloys, the presence of the eutectic necessitated a modification of the technique. To prevent the formation of a eutectic alloy by diffusion between the support wire and the samples, the osmium-rich specimens were rested within a small cavity in a disc of pure thoria, which in turn was placed in a cradle of thin tungsten sheet. The melting point of pure osmium, taken as the mean of two close determinations was found by this method to be $2970 \pm 15^\circ\text{C}$.

A new determination of the osmium melting point has also been recently made by KNAPTON, SAVILL AND SIDDALL¹¹ by direct measurement of the black body radiation from a hole near the center of an electrically heated bar. Their value is $3045^\circ \pm 30^\circ$ as compared with earlier values of 2500°C by TAMMANN¹², $2750 \pm 100^\circ\text{C}$ by FROHLICH¹³ and 3005°C by VINES¹⁴. It may be that our own determination of $2970 \pm 15^\circ\text{C}$ is slightly low owing to the possibility of reaction with oxygen liberated by the thoria which begins to develop an appreciable oxygen partial pressure at these extremely high temperatures.

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Book Review

Cobalt Monograph. Produced in collaboration with the staff of Battelle Memorial Institute, U.S.A. Edited by Centre d'Information du Cobalt, Brussels, 1960; 515 pages, 750 Belgian francs.

The main uses of cobalt have been firmly established for some considerable time but interest in this metal is active, especially in the advantages it has to offer in alloys for use at elevated temperatures. The appearance of this book is therefore most opportune. It summarizes in detail existing information on practically every aspect of the occurrence, extraction, properties, and uses of cobalt. While the metallurgy and metallurgical applications of this interesting metal are fully covered the book is not confined thereto; the chemistry of the metal receives full consideration along with its non-metallurgical applications, such as in glass and ceramics, in catalysis, in the paint industry, and in agriculture. Radioactive cobalt and its applications have not been forgotten and the final chapter of the book deals with the medical aspects of the metal.

This is an excellent book and those responsible for its compilation are to be congratulated on the success they have achieved in presenting so much valuable data in a single attractive volume. Although its publishers draw attention to possible omissions it would be difficult to find fault with the book in this or, in fact, in any other direction. Similarly, it is pointed out that no subject index is included but this omission is no disadvantage; the planning of the book is such that, with the aid of the extensive details included in its chapter contents, information can be traced with the minimum of effort. Those seeking still further information on specific topics are fully catered for by the very complete bibliographical references that accompany each chapter.

The book is strongly recommended to all who have an interest, however remote, in the important metal with which it deals.

J.W.C.

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